Landfarming of polycyclic aromatic hydrocarbons and mineral oil contaminated sediments

Stellingen

1. Na de afbraak van de snel afbreekbare PAK's is er geen waarneembaar verschil meer in de afbraaksnelheid van de resterende laag- en hoog-moleculaire PAK's. De waargenomen gelijke afbraaksnelheid voor de verschillende PAK's is in strijd met het algemene verwachtingspatroon met betrekking tot deze afbraak, maar wetenschappelijk te verklaren.

   Dit proefschrift.

   After degradation of the fast degradable PAHs, no difference in the degradation rate of the residual low- and high molecular weight PAHs is observable. This observed equal degradation rate of the different PAHs is in contradiction with the general expectation in relation to this degradation, but is scientific explainable.

2. De snelheid waarmee de acceptatiegrens voor minerale olie voor hergebruik van baggerspecie in de onderzoeksperiode is gestegen, is vergelijkbaar met de snelheid waarmee het minerale oliegehalte in gereinigde baggerspecie op Kreekraksluizen is gedaald. De aanpassing van de acceptatiegrens zal leiden tot onnodig en ongewenst hoge gehalten aan minerale olie in bouwstoffen.

   Dit proefschrift.
   Tijdelijke vrijstelling eisen grond en baggerspecie. Staatscourant 27 februari, 2004, nr 40, 25.

   The rate of increase of the acceptable concentration of mineral oil for reuse of sediment during the research period is comparable with the rate of decrease of the mineral oil content in remediated sediments on Kreekraksluizen. The adjustment of the acceptable value will lead to unnecessary and unwanted high contents of mineral oil in building materials.

3. Biologische saneringsmethoden voor verontreinigde (water)bodems die effectiviteit beloven en niet ingaan op beperkende factoren, moeten niet serieus worden genomen.

   Biological remediation technologies for soils and sediments that promise to be effective but do not consider limiting factors should not been taken seriously.

4. Het definiëren van de term 'bioaccessibility' als aanvulling op 'bioavailability' van verontreinigingen in (water)bodems kan nuttig zijn voor de wetenschappelijke discussie. Het maakt echter de discussie met beleidsinstanties over een normstelling gebaseerd op biobeschikbaarheid onnodig moeilijk.

   Semple *et al.*, 2004. Environ. Sc. Technol. 38, 228A-231A.
   ISO/CD 17924.

   Defining of the expression 'bioaccessibility' as addition to 'bioavailability' can be advantageous for the scientific discussion, but makes the discussion with administration officials on target values, which includes bioavailability, unnecessarily difficult.

5. Maatregelen in het kader van het Waterbeleid voor de 21^e eeuw houden te weinig rekening met de waterkwaliteit en kunnen daarom contraproductief zijn voor het realiseren van doelen van de Europese Kaderrichtlijn Water.

   Advies van de Commissie Waterbeheer 21^e eeuw, 2000. Waterbeleid voor de 21^e eeuw.
   EU, 2000. Kaderrichtlijn water, richtlijn nr. 2000/60/EG.

   Measures within the framework of 'Water Management for the 21^e century' do not take water quality sufficiently into account and will, therefore be counterproductive for realisation of the goals of the European Water Framework Directive.

6. Ontwikkelaars van dure en tijdrovende, maar wetenschappelijk goed onderbouwde methoden voor het vaststellen van risico's van verontreinigingen, moeten zich niet richten op een wijdverbreide toepassing van hun methode, maar op toepassing van hun kennis voor het vaststellen van het werkgebied van goedkope en snelle testen voor het meten van risico's

   Developers of expensive and time consuming, but scientifically defensible methods to establish the risks of contaminants should not focus on a widespread application of their method, but on application of their knowledge for establishing the scope of inexpensive and rapid tests for measurements of risks

7. De wetenschap kan slechts vooruitgang boeken door onderzoekers die over grenzen durven gaan. Zij die zich uitsluitend binnen de door managers en projectdiscipline vooraf aangegeven grenzen bewegen, zijn voor de echte wetenschap verloren (vrij naar Goethe).

   Science can only make progress by scientists who dare to pass borders. Those who only work within borders given by managers and project discipline are lost for real science.

8. Zoals weinig variatie in milieuomstandigheden leidt tot een eenvormige vegetatie en het ontbreken van vegetatietypen die in het oog springen, zal de huidige beperkte variatie in onderzoekssturing door de markt leiden tot verschraling van resultaten en uitblijven van echte innovaties.

   Similar to the conditions where small variation in environmental conditions produce monotonous vegetation without eye-catching types of vegetation, the present limited variation produced by market driven research will lead to poorer results and absence of real innovations.

Stellingen behorende bij het proefschrift 'Landfarming of polycyclic aromatic hydrocarbons and mineral oil contaminated sediments'.

Joop Harmsen
Wageningen, 22 november 2004

MISSION: Alterra is the main centre of expertise on rural areas and water management in the Netherlands. It was founded 1 January 2000. Alterra combines a huge range of expertise on rural areas and their sustainable use, including aspects such as water, wildlife, forests, the environment, soils, landscape, climate and recreation, as well as various other aspects relevant to the development and management of the environment we live in. Alterra engages in strategic and applied research to support design processes, policymaking and management at the local, national and international level. This includes not only innovative, interdisciplinary research on complex problems relating to rural areas, but also the production of readily applicable knowledge and expertise enabling rapid and adequate solutions to practical problems.

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Landfarming of polycyclic aromatic hydrocarbons and mineral oil contaminated sediments

Joop Harmsen

ALTERRA SCIENTIFIC CONTRIBUTIONS 14

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Abstract

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Key words: landfarming, sediment, polycyclic aromatic hydrocarbons, mineral oil, biodegradation, bioavailability, risks, target value, intensive, passive.

Due to the necessity of continuous dredging activities in the Netherlands, there is an enormous amount of contaminated sediments generated. These sediments require an efficient treatment procedure to reduce contaminant levels at low costs and with reasonable spatial demands. Landfarming offers a good solution for sediments contaminated with Polycyclic Aromatic Hydrocarbons (PAHs) and mineral oil. Sediments become aerobic during landfarming, which enables aerobic organisms to biodegrade the contaminants. Two main principles and types of landfarming are distinguished: (1) Intensive landfarming, in which processes are optimised using active management activities to reduce contaminants to residual concentrations as quickly as possible and (2) Passive landfarming, consisting of minimal management activities that are used when rapid bioremediation is not necessary, but residual concentrations of contaminants must be reduced.

PAHs and mineral oil are strongly ad- or absorbed by the organic matter in the sediment. Biodegradation of these contaminants in landfarmed sediment is shown to be a slow process and often high levels of residual concentrations are left. It is therefore important to understand limiting conditions for biodegradation. Limiting conditions that are discussed and mathematical described include (1) desorption and diffusion of the contaminant within soil aggregates to a place with active micro-organisms, (2) presence of active micro-organisms, and (3) aeration of the dredged sediment. The concept of bioavailability and its use to predict biodegradation and the risks during landfarming are also extensively discussed.

Landfarming of dredged sediment has been applied from 1990 onwards on the landfarm Kreekraksluizen in the Netherlands. From these long-term experiments it was possible to recognise fast, slow and very slowly degradable fractions of PAHs. The degradation rate constants of these fractions are derived from the measured data. To fully degrade these three fractions requires, respectively, 1 year, about 7 years, and 30-60 years. Optimisation of the degradation process (dewatering, temperature, aeration and activation of biological activity) only leads to an acceleration of the

biodegradation of the fast degradable fraction. Therefore, optimisation of passive landfarming is not effective in most cases.

Risks for the retention (ability to adsorb contaminants and to prevent mobilisation) and habitat (optimal functioning of soil living organisms) functions of the landfarmed sediments on Kreekraksluizen have been studied by measuring leaching, application of several bio-assays, and monitoring biological activity in general. Risks for the retention function decreased very rapidly during dewatering. The risk for the habitat function decreased more slowly. Small effects in bio-assays were still measurable after 7 years of treatment. No measurable risks were present in the longest (12 years) treated sediments.

As a traditional management practice, slightly polluted sediments from ditches in the rural area of The Netherlands are spread over adjacent land. In experiments on the island of Goeree-Overflakkee, it has been shown that the practise of spreading of thin layers also led to fast, slow and very slow degradation of the PAHs present. The historical practise of spreading had led to a small but stabilised increase, of the PAHs-concentration beside the ditches.

This thesis concludes with a description of the application of passive landfarming in real-world situations, as it is combined with nature development, used in construction, and combined with growing of biomass for energy production. The presence and effects of heavy metals are also discussed.

Contents

Preface

Sediments are often contaminated by Polycyclic Aromatic Hydrocarbons (PAHs) and mineral oil. Fortunately the sediment can be cleaned by micro-organisms that are able to degrade these contaminants. This thesis describes the applicability of landfarming to clean PAHs and mineral oil contaminated sediments. Some results described in this thesis were published previously and presented at several (inter)national symposia. The idea of summarising and re-evaluating all of these results was developed after discussion with my promoter Wim Rulkens, co-promoters Ronald Sims and Herman Eijsackers and my former department head Pim Rijtema. Their stimulation has not only led to a useful summary of previous material, but also to a critical discussion of all current material. This has resulted in the development of improved insights in relevant processes and also new ideas for identifying limiting processes for biodegradation of contaminants using the technology of landfarming.

Important in this study was the landfarm on Kreekraksluizen where landfarming was investigated in cooperation with RIZA (Lelystad, the Netherlands). Landfarming processes were investigated during a period of more than 10 years, which made it possible to predict the effect of landfarming in the long term. The data base for this site is unique and will be extended in the future. The large experimental research on Kreekraksluizen was supported by several studies at other sites and in the laboratories of Alterra.

This thesis could not have been written without the support of a lot of persons and institutions. Starting with the institutions, I would like to acknowledge my own institute Alterra for the support during the work of all the different aspects treated in this thesis. Most work was carried out within programs of the Dutch Ministry of Agriculture, Nature and Food of the Netherlands in combination with research programs of the Dutch Ministry of Water Management and Traffic, led by RIZA (Lelystad, The Netherlands). Parts of the research were supported by the Water board of Goeree-Overflakkee, NOVEM and NOBIS.

During the writing of this thesis, I was criticised and supported by my promoter Wim Rulkens and co-promoters Ronald Sims and Herman Eijsackers. Discussions with them, in their own offices and also at other places around the world, were very stimulating.

A special acknowledgement is extended to Pim Rijtema. He was a driving force in starting this work. He also took his responsibility and supported me in the development of some theories to explain processes occurring during landfarming, and in the development of predictive models. We could do this using the mental support of Wil Rijtema.

This work could not have been started and continued without the cooperation of colleagues of RIZA, where Marijke Ferdinandy had a special position of support. Within good and bad periods she always found ways to continue the work and to incorporate related subjects. Her successors Leon de Poorter and Leonard Osté continued the good cooperation. As a result, landfarming of sediment is now considered as one of the proven applicable technologies.

In Chapter 3 on bioavailability I used results and ideas (1) developed in a SETAC-Pellston-workshop together with Martin Alexander, Rufus Chaney, Scott Cunningham and Joseph Hughes, (2) developed during writing a chapter for a book together with Paul Frintrop and (3) developed during meetings of the Working group Bioavailability of ISO/TC190 Soil Quality.

In an institute you do not work alone. Good results can only be obtained with a good team. My direct colleagues Hans Zweers, Antonie van den Toorn, Delia van Dijk-Hooyer and Rick Wieggers were involved during the whole or part of the research period. Other colleagues were involved in specific parts of the study. I would like to acknowledge, Jan van den Akker, Jaap Bloem, Jos Bodt, Dethmer Boels, Dick Brus, Luc Bonte, Lucas Bouwman, Bertjan Groenenberg, Jan Japenga, Wim Ma, Jaap Pankow, Paul Römkens, Wobbe Schuurmans, Jannes Stolte, Meint Veninga, An Vos, Bram de Vos and Wim de Vries.

At the end of this study, Judy Sims and Harrie Bosman read and commented on the last version of several chapters, Martin Jansen made and improved the figures and Henny Michel, Ans van Dillen and Jobbe Wijnen improved the lay out. My daughter Evelien and Martin Jansen designed the cover of this thesis, making use of the etching 'Joop Harmsen' made by Lia Stouten in the series GrafischProject 2000 (www.liastouten .nl).

During a period of more than 10 years you met and talk with many scientists that influence your thinking. It is impossible to give a complete list and therefore I want to thank them in this way and I hope they continue in the free exchange of knowledge, which is essential to improve the environmental quality of the world.

Last but not least: my wife Wilma, my daughters Mijke (including her boy friend Niels), and Evelien and my son Leander, who did not always like the time I spent on this work, but are also proud on the end result. This book is dedicated to them.

The research described in this thesis is based on experiments on (semi)field scale. There are no special regulations for these types of experiments in the Netherlands and therefore regulations applicable for large-scale handling of contaminated sediments and soils are required to be used. The experimental research described in this thesis was not always in agreement with these regulations. Having in mind the pronouncement of Goethe 'Die Welt kan nur durch die gefördert werden die sich nicht entgegensetzen. Wer sich ihr anpasst ist für alles richtiges leben verloren', the experiments were conducted and the results are described and used in this thesis.

As described further in this thesis, we had to stop activities on Kreekraksluizen after it became known that one of the sediments, Petroleum Harbour sediment, was too contaminated to be transported from one province to another. The sediment was considered as chemical waste. We were unaware of this rule and had transported the sediment without permission. Although we had some delay after the breach of the rules was recognised, it was fortunately possible to continue and it is now possible to conclude that it is even possible to bioremediate sediments that have to be classified as chemical waste.

On Kreekraksluizen, it was prescribed to use a liner to prevent leaching of contaminants. Theoretically it could be shown that not applying a liner should be more effective for dewatering and that the amount of original organic matter or adding of extra organic matter could be effective as a filter for contaminants that leached. Doing such an experiment was not possible within the existing regulation and the procedure to get permission could take several years. Application of organic matter for soil protection was done on a small-scale (5x5 m). The liner on the bottom of this experimental field was replaced by the organic matter filter. To have sufficient capacity, the original soil had been enriched with organic matter (compost) and the quality of the leached water was measured (Chapter 7). Based on the results of this research, it was possible to work without liners on practical scale on Kreekraksluizen and on the Oostwaardhoeve where landfarming is applied on real large-scale (30 ha).

One of the experiments that involved the addition of substrate with fungi was carried out in the province of Limburg. Because Petroleum Harbour sediment had to be used, official permission for transport was necessary. This would take time, which was not available, and it was not certain if this permission would be given due to the regulations described before. The permission issue was overcome by transporting 100 buckets with 10 l of sediment samples instead of 1 m^3 of contaminated sediment. With this research it could be shown that intensivation of the treatment using fungi (Chapter 6) did not have any effect.

For the experiment that involved the spreading of sediment on Goeree-Overflakkee (Chapter 8) we were allowed to spread class 2 sediment (PAHs < 10 mg/kg d.m.). When controlling the quality of the sediment to be used, it was found that the present concentration was 15 mg/kg d.m., and therefore was too high to be used (class 3). Fortunately there was an analysis report available in which it was reported that the concentration was about 8 mg/kg d.m. This report was not older than half a year and could be used as a justification to start the experiment. After spreading of the sediment it was found that characterisation as class 3 sediment was correct. The experiment had demonstrated that spreading of sediment is a good management method to bioremediate slightly polluted sediments.

In the same experiment with 80 m^3 of sediment, it was necessary to fill in forms required by the authorities for a large deposit of thousands of cubic meters. Collecting the proper data for the forms would have required an unbalanced input of time and ultimately not all of the information requested was available to the authorities. They did not reply and the experiment was completed as planned.

All these examples demonstrate that it is necessary to have some regulatory flexibility for doing experiments. If research to generate new developments is judged on regulations for old technology, it will prevent the development of new concepts for improving the environment.

1 General introduction

1.1 Introduction

Good soil quality and water quality are important for life and the basis for a high biodiversity. Soil and water systems are essential for a sustainable way of living. Biological waste is a product of life and in sustainable and healthy systems waste products such as dead organisms and excrements become part of these systems. They even stimulate microbiological life and the growth of vegetation. Human activities have influenced the soil system and agriculture practise has changed large areas in such a way that a desired soil system is obtained producing the food essential for the survival of the human population. These activities have not only changed many soil systems, but also water systems. Waste in the form of manure is necessary to maintain such a system. Without this active change of the soil system, the earth would not be able to feed 5 billion people.

Human activities, however, can also be a threat for the soil and water system and destroy their function in natural and desired life cycles. Many hazardous substances are used in such amounts and concentrations that they may harm the soil and water systems. After introduction or disposal of these hazardous chemicals in soil and water, the soil, water and sediment become polluted and may not be able anymore to fulfil all its original functions. In the Western countries, building a large number of sewage treatment plants from the beginning of the 1960s has solved water pollution. Soil pollution was recognised as a serious problem in the 1970s. At first attention was given to the heavily polluted sites like landfills and industrial sites. In these situations the negative effect of the contaminants was undeniable and visible for everybody. It took more time to realise that also diffuse pollution might influence the desired role of the soil system. Specialists could only measure effects, like lower biodiversity and crop quality. In a densely populated country like the Netherlands it is not accepted by society that large areas are too polluted to function properly. Polluted soils have to be treated in such a way that the soil can fulfil a useful function. The functionality of soil should be as high as possible. Complete removal of contaminants results again in a multifunctional soil, which can be used for its original but also for other purposes. If this is not possible, the functionality may be limited to a few number of functions, hopefully including the original function, or even to very limited functions like increment soil in roads.

To distinguish the degree of pollution, the Dutch government developed the A-, B- and C-values in the late 1970s (Moen *et al.*, 1986). The A-value was for heavy metals equal to the background value and for organic contaminants equal to a presumed harmless concentration or the chemical-analytical detection limit of these contaminants. Above the C-value the soil was considered to be strongly polluted and the soil should be remediated. The B-value was in between and measures, necessarily to control the contamination, depended on the local situation. Pollution was considered as a reversible process. If a site was polluted it had to be cleaned until the A-value was reached again. After remediation the soil must be available for every form of soil use and natural function, typical for the specific soil. This 'multifunctionality' was the leading principle in the Dutch soil regulation. Multifunctionality was expressed as the A-values of the principal contaminants as heavy metals, mineral oil, Polycyclic Aromatic Hydrocarbons (PAHs), solvents and (agricultural) chemicals. In 1994 The A-, B- and C-values were replaced by the reference and intervention values (VROM, 1994). The new values were more ecotoxicologically supported (Lijzen *et al.*, 2001). The reference value was comparable with the old A-value and the intervention value comparable with the old C-value (see Table 1.1). Concentrations in Table 1.1 are given for standard soil (10% organic matter and 25% clay). For the organic contaminants, PAHs and mineral oil, only organic matter has to be considered and normalisation means multiplying of the measured value with 10/(percentage organic matter).

Sediments were also shown to be polluted. They acted and are still acting as sinks for many contaminants entering the water phase. Serious pollution has been recognised in harbours and industrial areas, but also sediments in rural areas were polluted. In the Netherlands, but also in other countries, it is necessary to dredge water systems in order to assure the accessibility of harbours and the proper functioning of the smaller channel and ditch system for supply and discharge of water. Several studies have shown that there is a large amount of polluted sediments, but discussion on exact amounts is still going on. In a report on the sediment issue in the Netherlands (AKWA, 2001) it was concluded, that it will take until the year 2010 to treat about 250 million cubic meters of slightly to heavily polluted dredged sediment present in water ways in The Netherlands.

For polluted sediments a slightly different assessment system than used for polluted soil has been developed in The Netherlands. Five classes are distinguished, as illustrated in Table 1.1 for the contaminants PAHs and mineral oil. Sediments in class 3 and 4 have to be treated and sediments in class 0 and 1 are considered to be clean or clean enough for all soil uses. Class 2 can be reused with certain restrictions. Concentrations in Table 1.1 are given for standard sediment (10% organic matter and 25% clay).

Table 1.1 Classes of contaminated sediments and soils (standard sediment, 10% organic matter and 25% clay).

Class	Degree of pollution	Limits (mg/kg d.m.)	
		PAHs	Mineral oil
Soils[1]			
Reference value	Clean soil	1	<50
Intervention value	Heavily contaminated	>40	> 5000
Sediments[2]			
0	Clean, reference value	<1	<50
1	Clean - slightly contaminated	<1	50-100
2	Slightly contaminated	1-10	100-3000
3	Medium contaminated	10-40	3000-5000
4	Heavily contaminated	>40	>5000

[1] VROM, 2000

[2] Staatscourant, 2000

It was generally considered that cleaning of soil and sediments could be achieved using technology. Several technologies were developed to remove (destruction or extraction or biodegradation) the contaminants from the soil. Treatment times had to be short, preferably days or weeks. As long as the final concentration became smaller than the A-value, the technology was suitable. The use of very soil-life destructive methods was sometimes necessary to reach this goal. For organic contaminants thermal treatment became the most popular method, because with other less destructive methods residual concentrations were above the target value.

Treatment for contaminated soil and sediment strongly depends on government regulations, social and administrative acceptance, and technological know-how. All these factors are subject to changes over time (Harmsen and Hoeks, 1998). In the 1980s and early 1990s, complete removal of the contaminants or isolation of polluted soil and sediments in disposal sites were the only available possibilities. Only relative small amounts of soil polluted with easily degradable contaminants were bioremediated.

From 1996 onwards bioremediation became an issue again in The Netherlands. There were two reasons: a change in policy of the government (Deelen and Roels, 1997), which resulted in renewal of the policy on contaminated soils, known as BEVER (SDU, 1999), and the stimulation of research and application by the Dutch Stimulation Programme Biological In-Situ Remediation (NOBIS, 1997). The change of the policy was drastic, for it was accepted that complete removal was not always possible, and limited but functional use instead of multifunctional use became possible. It was not necessary anymore to remove all the contaminants but higher residual concentrations (set in new target values, see also Section 1.2.3) were allowed, providing prescribed precautions are applied and use of the soil is limited.

Prevention of pollution and functional remediation, in which a low concentration of the contaminant is accepted is replacing complete removal of the contaminant and isolation, as mainly applied in the technology approach. Biological methods play an important role in these functional remediation methods. Several natural, mainly biological, processes are responsible for the biodegradation of contaminants in the soil. These processes occur in healthy and in polluted soil systems and enable recovery. It may be necessary to give some assistance, but most of the work has to be done by soil life itself. Using the natural recovery system, the negative effects of contaminants will decrease in the long term.

In this thesis, biological treatment by landfarming is described to remove the organic contaminants PAHs and mineral oil. It is restricted to pollution in sediments, which represent an important part of the environmental problems in The Netherlands. The goal of this biological treatment system is to recover the polluted sediment completely or to such a degree that the sediment can have a limited but functional reuse. Landfarming, which is described further in this general introduction, is currently the most important biological treatment system. It is a cost-effective technology that can be applied on large scale. For field scale application it is necessary to understand all limiting factors that have influence on the field scale rate of biodegradation and the ecotoxicological effects. This has to be supported with field data. In this thesis data are presented of sediments landfarmed starting from 1990. Using these data it was possible to derive real degradation rates and to show the decreasing ecotoxicological effects during remediation. Knowing limitations and degradation rates it is possible to predict the quality improvement of sediments during treatment on a landfarm. The same knowledge can be used to predict soil quality when sediments from ditch systems are directly spread on agricultural land, as is common practice in The Netherlands for slightly contaminated sediment (class 2) and to develop applications of landfarming in combination with functional use of the applied area.

1.2 Development of landfarming

1.2.1 From waste treatment to soil treatment

During the 1970's, oil-containing waste from the oil industry in the United States was disposed by mixing it with soil (Dibble and Bartha, 1979). It is estimated that in 1973 less than 10% of facilities with oil refinery sludges utilized land treatment, and by 1979 from 34% to 50% of refinery facilities used land treatment (Arora *et al.*, 1982). In 1986 it was reported that there were few definitive data in the literature quantifying waste biodegradation rates in full-scale land treatment systems (Huddleston *et al.*, 1986). This technique, referred to as sludge farming, was considered effective for the treatment of refinery waste. During this period the environmental impact of this type of waste management on the long-term behaviour of soil and groundwater resources was not a primary design, management, or performance criterion. In 1979 Dr. Michael Overcash stated that "… land application is not viewed as a technology by industrial waste engineers, but rather as a nondescript system of irrigation or spreading. The lack of firm design criteria has made land treatment the equivalent of shovelling smoke" (Overcash and Pal, 1979).

In the decade from 1980 to 1990 design of land treatment systems in the U.S. for industrial wastes classified as hazardous waste was based on regulatory mandates of the Resource Conservation and Recovery Act (RCRA, 1976). Requirements of the regulations specified that to obtain a permit it must be demonstrated that any hazardous constituents contained in the waste to be land applied must be degraded, transformed, and/or immobilized in the soil treatment zone, generally considered to be the upper layer (1.5 m) of soil (U.S. EPA, 1986).

An important design criterion that recognised the sustainability issue for soil restoration was identified in 1979, and was based on the constraint of nondegradation or nondecline of the soil through determining the Soil-Site Assimilative Capacity (SSAC) for each target chemical in a waste. That is, the waste when considered on a constituent-by-constituent basis is applied to the plant-soil system at such loading rates and frequencies, and over such limited time spans, that no land is irreversibly removed from some other potential societal usage such as forestation, agriculture, and development (Overcash and Pal, 1979). These design issues were developed within the context of ensuring protection of public health and the environment. The nondegradation constraint and the determination of SSAC for target chemicals were used as the basis for development of the U.S. Environmental Protection Agency Permit Guidance Manual on Hazardous Waste Land Treatment, published in 1986 (U.S. EPA, 1986). Land treatment of hazardous waste was banned in the late 1980s because it was defined as a form of land disposal without pretreatment, rather than recognised for the treatment and sustainability bases that guided the design, management, and performance of land treatment units in the early 1980s (U.S. EPA, 1987).

The knowledge on biodegradation of mineral oil was used for cleaning of polluted soils on pilot scale in landfarms in The Netherlands (Hoeks *et al.*, 1988). Laboratory research was done to support the pilot studies. The public response to biodegradation of polluted soils was positive and biodegradation appeared to be the solution for mineral oil polluted soil.

In the decade from 1990 to 2000, the emphasis in the application of hazardous waste landfarming technology further evolved from treatment of industrial liquid and sludge wastes to treatment of contaminated soil, not only in the U.S., but worldwide.

In the U.S., contaminated soil identified under the U.S. EPA Superfund program, titled the Comprehensive Environmental Response, Compensation, and Liability Act of 1980 (CERCLA) was frequently remediated to target cleanup levels using landfarming technology (Sims, 1990, Sims *et al.*, 1990). A more detailed summary of the practices and effectiveness of landfarming technology in the treatment of petroleum contaminated soils were presented by Sims and Sims (1999). Often, however, the target levels for cleanup identified in the Records of Decision under CERCLA did not consider the design and performance constraints necessary for sustainable restoration of soil (Sims et. al. 1996).

In 2000, a re-focus on the sustainable restoration of contaminated soil occurred at the NATO Advanced Research Workshop (Sasek *et al.*, 2001). The topic of the conference was the utilisation of bioremediation to reduce soil contamination. The topic of using the landfarming framework for soil bioremediation emphasised the importance of designing and operating soil bioremediation systems with the goal of achieving sustainable restoration of soil based on the nondegradation constraint and SSAC described previously (Sims and Sims, 2001).

Landfarming for accomplishing sustainable restoration of soil is a technology based on the utilisation of soil micro-organisms and sustainable agricultural methods in an aerobic environment to treat soil contamination through transformation, immobilisation, and detoxification processes in order to protect public health and the environment. Sustainable landfarming should accomplish as far as possible recycling of natural organic carbon and nutrients within the biosphere and it should maintain basic soil characteristics necessary to support plant growth (forestation, vegetation, etc.), and thus contributes to environmental natural resource sustainability and economic utilisation of restored land. The success of landfarming technology with regard to remediation of contaminated soil depends upon efficient utilisation of micro-organisms in a soil farm environment to treat soil contamination while recognising limited conditions for biodegradation.

1.2.2 Landfarming of sediments

In The Netherlands, large amounts of sediments are slightly to heavily polluted. Main contaminants are Polycyclic Aromatic Hydrocarbons (PAHs), mineral oil and heavy metals. Anaerobic conditions in sediments are responsible for the absence of PAHs- and mineral oil degradation and strong binding of heavy metals. Measuring PAHs in dated sediments (1965-1998) and using a chemical mass balance model Li *et al.* (2001) concluded that no degradation of PAHs occurred in the investigated sediments. Therefore, contaminants present in the sediment will not leave the sediment and the degree of pollution will increase in time by new contamination. Sediment can be considered as a sink for pollution. In a delta area like The Netherlands new sediments are formed continuously and as long as contaminants are released into the environment, these new sediments may be polluted. Model studies (Kramer *et al.*, 1997) have shown that in the Dutch situation release of the main contaminants will remain on such a level that polluted sediments are to be expected for the next hundred years, so there must become a way to handle the large amount of polluted sediments.

Cleaning of the millions of cubic meters of polluted sediments in the coming years can only be achieved if inexpensive technologies are available. Separation of clean sand from sand rich polluted sediment is the most used, cost-effective technology. Based on research results also described in this thesis, landfarming is considered as a promising inexpensive technology (Ringeling and Rienks, 2001; AKWA, 2001) to remediate sediments contaminated with PAHs and mineral oil. The application of landfarming technology changes sediment (contaminated as well as clean) into soil, which is a process that has resulted in fruitful soils in the polder areas, and has assimilated sediment from ditches to become part of the agricultural soil. Within this context, landfarming is applicable for the removal of contaminants through bioremediation of sediments and the product of landfarming, a soil, can be reused.

The Netherlands is the delta system of some major European rivers, the Rhine, Meuse, and Schelde. These rivers transport large amounts of sediment, which will precipitate in areas with lower flow velocities (harbours and lakes). To keep these areas accessible for ships, regular dredging is necessary. When these dredged sediments are polluted with biodegradable contaminants, landfarming can be used to remediate them. With a high water discharge by the river and resulting high water table, sedimentation also occurs in the floodplains of the river systems. This sediment was clean until the industrial revolution in the nineteenth century. Up to the 1970s it has become more polluted, but fortunately the quality has been improved significantly in last decades. The floodplains are one of the largest diffuse polluted areas of the Netherlands. They are in use as agricultural area, for nature development but also for recreation. The floodplain landscape is typical for The Netherlands. The average sedimentation is 1 mm per year. This reduces the discharge capacity of the complete system (river + floodplains) in time. With the extremely high water periods experienced in 1995 and 1996, this has lead to critical situations and now a big program 'Space for the river' has been started. Large excavations of sediments in the floodplains are necessary. The pollution in lower soil layers, however, may hamper this development. Lessons learned from landfarming can be used to handle these sediments in such a way that the quality will improve in time.

1.2.3 Impact of target values

Landfarming treatment through bioremediation can be measured and reported in several ways, including percent of contaminant reduction, comparison with target cleanup concentrations, and/or residual risk to human health or the environment. Different standards exist in different countries and different geographical areas. For example, in 1991 landfarming of soil polluted with initial pentachlorophenol concentration of 100 mg/kg d.m. to reach a final concentration of 10 mg/kg d.m. could be considered a success in Canada because a reduction of 90% was achieved. However this would be considered as a failure in The Netherlands because the target value was not achieved. Risk-based criteria and the use of the soil following landfarming treatment will become increasingly important in soil remediation, similar to the goal of treating industrial wastes with landfarming using the nondegradation design constraint and the SSAC concepts.

In most countries the residual concentration present after landfarming was accepted. Unfortunately this residual concentration is often higher than the A-value used in The Netherlands as target value. All the contaminants had to be removed and a residual concentration equal to the natural background was only allowed. Only when using bioremediation of volatile mineral oil products such as gasoline and kerosene under optimal conditions, successes were obtained by degradation to levels below the A-value. It was necessary that contaminated soil and sediment had to be cleaned to address the criteria for multifunctional use, which required treatment to 50 mg/kg d.m. mineral oil and 1 mg/kg d.m. PAHs. With contaminants like heavy oils and PAHs the target of producing a multifunctional soil (= aiming at lower than A-value) was not reached. Especially the PAHs presented a problem. However degradation does not stop after removal of the bioavailable fraction, but continues at a greatly reduced rate and will lead eventually to lower concentrations. The bioavailable fraction is the fraction of the contaminant that is degraded during the treatment on the landfarm. The concept of bioavailability is further discussed in this thesis (Chapter 3).

Multifunctionality as the guiding principle for remediation of polluted sites was replaced by introduction of a renewal of the Dutch policy on contaminated soils, BEVER (SDU, 1999). In the Building Material Act (Staatsblad, 1995), criteria for reuse of (treated) soils and sediments as building materials are described that allowed higher residual concentrations. Results of remediation were no longer assessed on the basis of multifunctionality, the treated soil or sediment could also be assessed on its functionality as building material. As long as the concentration was below a set value and there was no danger for leaching, the soil or sediment could be reused. Prescribed leaching tests controlled the use of treated soil and sediment. For PAHs the consequences were considerable. Before the Building Act it was necessary to clean the soil or sediment to a residual concentration of 1 mg/kg d.m. This was a 'mission impossible'. The new value of 40 mg/kg d.m. was more realistic and provided a major stimulant for the application of bioremediation.

Using these criteria, restricted use of remediated soil and sediment became possible. Cleaning by landfarming using intensive techniques became effective, and as a result bioremediation became more popular. In Figure 1.1 the consequences of the changing policy are given, presenting the PAHs degradation curves of sediments from the Geul Harbour and from Zierikzee in a landfarm (see also Chapter 4). Using the former multifunctional target value, only the PAHs-concentration in the Geul Harbour sediment approaches the reference value. For the Zierikzee sediment it is clear that several more decades will be necessary. With this target value, landfarming will only be effective for a limited number of polluted soils or sediments. With the new target value for building materials, the situation is completely different. Already in the first year the target value has been reached and this situation will occur for many polluted soils and sediments.

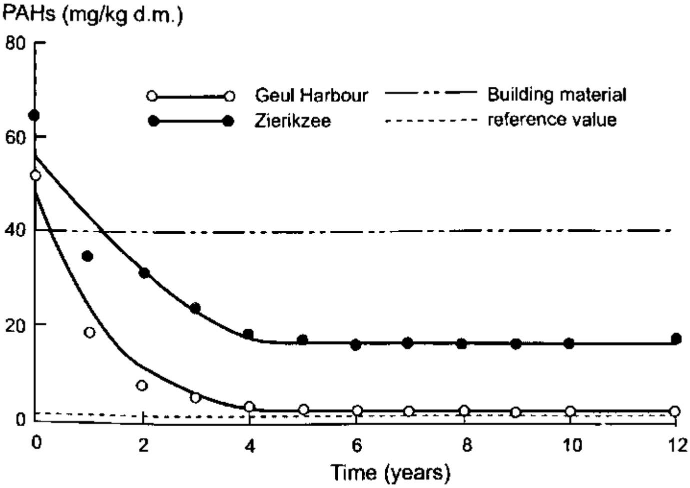

Figure 1.1 Degradation of PAHs in Geul Harbour and Zierikzee sediment on a landfarm. The horizontal lines are target values from the Multifunctionality Approach (reference value) and the Building Material Act.

Unfortunately mineral oil in sediment often slowly degrades in a landfarm (see also Chapter 5). With the Building Material Act, the critical contaminants are not the PAHs, but mineral oil. In general, 3-6 years of landfarming are necessary to achieve a value of 500 mg/kg in sediments. Until 2004 the time required to achieve the target concentration for mineral oil was the controlling factor in the length of treatment time required for polluted sediments. Therefore mineral oil is the 'land limiting constituent (LLC)' for polluted sediments (Overcash and Pal, 1979). Fortunately this has also a positive influence on the quality of the treated soil. The longer treatment time results in soil with a PAHs-concentration far below the target value for building material. The level of the residual concentration will be reached and the bioavailability of this rather stable concentration is low. This has to be regarded as a positive environmental effect. The change of the target value for mineral oil in treated sediments to 2000 mg/kg d.m. as decided in 2004 (VROM, 2004), will result in shorter treatment times and more biodegradable PAHs will be present on the reuse locations.

Many soils and sediments have PAHs-concentration levels between the reference value and the value for building material. Soils or sediments from small sites are directly, or after a short physical treatment of a few months, usable as building material. However, for diffuse polluted sites, for example, the flood plains of the River Rhine, this would not be an acceptable solution. These sites are very large and excavating should create a large mountain in the flat Dutch landscape. On these sites also a more multifunctional use (nature development) is the wish of the community and the goal of treatment. In these cases the principles of multifunctionality still play a role. Remediation will be necessary until a harmless, but also acceptable residual concentration is achieved.

As mentioned previously, the application in policy of the concept of multifunctionality hampered the use of landfarming in the Netherlands for a long time. Therefore, it should be realised that the development of landfarming is not only influenced by development of technology but also by target values set by the government. For a long time research was focussed on the means to decrease the residual concentration in a technical way, so that a low residual concentration could be obtained in the short term. Activities were focussed on the improvement of aeration and the presence of degrading micro-organisms. As a result, the principles of landfarming were better understood, but the target value defined by multifunctionality could not be reached yet. Fortunately it was possible to carry out long-term experiments as described in this thesis, and application became only possible after the mentioned change in policy of the government.

1.3 Developments in research

Landfarming is a method for aerobic biological treatment of contaminated soil and sediments. Its development has been influenced and will be influenced by all other research fields having relation with bioremediation of both soil and sediment. It is important to realise that development of knowledge may change opinions. In 1983 Sims and Overcash concluded:

'PAHs decompose in soil systems, probably more rapidly than in any other waste management alternative or receiver system involving biological activity. Research is needed to establish conclusively rates of decomposition and soil levels above which application of PAHs constituents adversely affect

the food chain. Thus utilisation of a soil assimilative capacity concept will allow treatment of PAHs compounds in an environmentally acceptable and cost-effective manner. Research must be initiated to study enhancement factors that increase degradation rate of PAHs especially those with more than three rings. Such research would not only add to present knowledge of PAHs decomposition pathways by soil micro-organisms under environmental conditions, but may also substantially increase the soil assimilative capacity and provide land application as an alternative technology that may be the most economical for safe and acceptable disposal of PAHs wastes".

At first sight, these conclusions could be considered still applicable, and the results of this thesis could be a reaction towards these conclusions. Several studies of and applications of bioremediation still have the goal to increase the degradation rate. The Sims and Overcash paper is still an important point of reference, but things have changed in the last two decades. In 1983 Sims and Overcash thought, like many others, that it was possible to increase the degradation rate, for example, by bacterial seeding, and that the soil system could even be used to clean up amended wastes. In the 21st century this thinking has been changed (Sims and Sims, 2001; Sims and Harmsen, 2001) and it is almost common knowledge that after the first fast degradation phase, a residual concentration is left that is considered persistent or slowly degradable, as will be demonstrated in this thesis. It is important to understand the presence of a residual concentration and its slow degradation rate for the proper use of bioremediation and in relation to possible negative environmental effects of the residual contaminants.

The landfarming process has been optimised by using tillage to enhance aeration, by adding nutrients, by enhancing temperature (Martin *et al.*, 1986, Nieman *et al.*, 1999) and by modelling the processes in the landfarm in order to predict effects of optimisation (Freijer, 1994, Kivanç, 1999). Optimisation techniques are applied in order to decrease treatment time required to achieve target soil concentrations. The most successful optimisation will lead to a bioreactor or slurry reactor in which the desired biodegradation will occur within days or a few weeks. Types of optimised landfarms may include fixed bed, biopiles, compost beds, and greenhouse farming systems. In the USA all of these landfarming technology-based systems are considered as different technologies. In The Netherlands these are considered as different ways of applying landfarming technology, and distinction is made with regard to intensive versus passive methods of landfarming. Intensive (proactive and aggressive) landfarming has been used to address high concentrations of easily degradable contaminant types for treatment in a shorter period of time. For example, companies in The Netherlands are exploring greenhouses or halls in which mineral oil polluted soils are cleaned within several months by utilising amendments and active landfarming; this is in comparison to the passive landfarming described in this thesis.

If a contaminant is present in unavailable matrices such as tar or plastic particles, bioremediation will not have much success. Bioremediation is possible if contaminants are distributed in soil or sediment and adsorbed as individual molecules or thin films. A bioremediation process can be optimised in order to increase the degradation rate of the process. It is known that a residual concentration of the contaminant is still present after treatment. This amount is said not to be available for the organisms responsible for the degradation, i.e., the bioavailability is low. Limited bioavailability was first explained by ad- and absorption of the contaminant in the soil matrix in such a way that it could not be reached by micro-organisms. This was a theoretical approach but also a useful concept. It could be used to convince people that a long time would be necessary to decrease the residual concentration. This was another way of thinking: when a contaminant is not available for degradation, it first has to become available by diffusion to a site with an active population of micro-organisms. These diffusion or desorption processes may take a very long time. Therefore it was better to distinguish landfarming in intensive landfarming, to quickly remove the bioavailable part of the contaminant load, followed by passive[1] landfarming for slow removal of the residual concentration. These slow processes make an intensive and optimised treatment not the wisest choice. Treatments with a low labour and energy input (passive) will be cost effective, especially if bioavailability is the determining factor (Harmsen, 1991, 1993 and 1999).

As long as bioavailability was a concept, it was only useful to understand the slow process of degradation. However, when the application of sorption models became possible, predictions of desorption followed by degradation could be made. Starting with a description of the interaction of organic contaminants in the soil/water system by chemical equilibrium (Mackay *et al.*, 1985), the deviation of non-equilibrium behaviour has been explained by introduction the process of diffusion in soil particles (Wu and Gschwend, 1986). The awareness of the presence of different forms of organic matter makes it also easier to understand slow degradation. The effect of tar particles on the degradation rate will be clear, but natural organic matter is also present in different forms. Organic matter can be described as an amorphous (gel-like) phase and a condensed more crystalline phase (Weber *et al.*, 1992; Pignatello and Xing, 1996). Not only the adsorption coefficient of the contaminant to the condensed organic matter can be larger, but also the diffusion through the condensed phase to degrading organisms can be slower.

Another important change was the development of methods to measure bio-availability. Different methods became available and the results could not only be used to predict biodegradation but also to predict (eco)toxicological effects and to measure desorption rate constants (Cornelissen *et al.*, 1997).

The process responsible for the slow degradation can be described as a theoretical concept, but also mathematically. A mathematical description remains a theoretical concept as long as it has not been validated with practical results. In this

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[1] In the Dutch language the expressions 'intensief' and 'extensief' landfarming are used. The English word 'extensive' may lead to confusion and passive landfarming is used in this thesis.

thesis, results of passive, more natural, treatment methods are described. The study on the landfarm near Kreekraksluizen in the province of Zeeland provides important results. This study was started in 1990, resulting in a database of more than 10 years. Already in 1994, a year that there was still believed to be a breakthrough on improving the bioavailability, a passive treatment was started. This database makes it possible to evaluate different theoretical approaches regarding the slow bioremediation process.

1.4 Application of landfarming

1.4.1 Biodegradable contaminants

To give landfarming an optimal role in sustainable use of resources the following items should be taken into account; 1) Money; 2) Space; 3) Time; 4) Energy; 5) Emission; 6) Use of raw materials (nutrients); 7) Depletion of non renewable materials; 8) Reuse; and 9) Public acceptance. The first 7 items should be as small as possible, and the last two as large as possible. Sustainable means searching for the most optimal approach in relation to all. For instance, it will not be possible to minimise all of the first 7 items. Comparing all factors will be difficult and depending on the situation, use of different weight factors may be necessary. With the context of different goals (target values) for sustainable landfarming, including residential and industrial reuse of site, nature development, agricultural use, and building materials, this technology will continue to be used in several ways. These uses are based on the desired target values in relation to reuse. In sustainable landfarming, this should be combined with knowledge on the maximum obtainable result. Prediction of this result becomes easier as described in this thesis. Knowing target values and the items described above, an appropriate way of landfarming can be chosen (Figure 1.2).

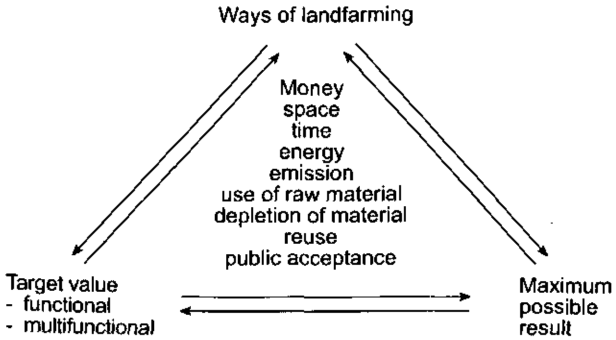

Figure 1.2 Factors having influence on the way of landfarming.

Intensive Landfarming to produce an industrial product. Several soil cleaning companies use landfarming as a production process; that is, they produce clean soil for multiple purposes. Because of the extended time requirements to reach criteria for multifunctional use, the focus of industrial treatment companies is on the target cleanup value for limited reuse of soil. Based on industrial process criteria of consistency of treatment, rapid treatment, and predictability of product quality, such companies utilise soil treatment optimisation techniques to achieve the most rapid treatment. Reduction of the time required for cleaning the soil to target levels is the most important tool for reducing costs within the industry. Nonetheless, for some soils, even optimised sustainable restoration may require several months to one year.

Landfarming with flexible time and cleanup constraints. Companies or communities with available space and without time pressure for development of the contaminated site may not need industrial assistance to remediate contaminated soil using landfarming. In this case an efficient or optimised process is not a criterion. The assurance that a community or company is developing requires that target levels for intended use should be reached in a timeframe that is generally less than 5 years. Due to this still limited time, they may reuse the soil as building material in future projects. The available time for treatment is generally not sufficient to reach criteria for more multifunctional uses of restored soil.

Landfarming as a natural process that supports vegetation growth. In the passive mode of landfarming, optimisation of the process is not the priority, and bioavailability is the limiting factor. The soil is required to be on the landfarm for treatment for an extended period of time, due to the low target levels for sustainable restoration and the limited bioavailability of the associated target chemicals. Intended uses include development of natural vegetation or special vegetation. In the Dutch situation with high costs for land, long treatment times will lead to a very expensive treatment technology. From a social point of view it is also not acceptable to use large areas of land in order to clean large quantities of contaminated soils and sediments. It is therefore necessary to combine landfarming with another profitable use of the used area. Combination of landfarming of sediments with the growth of biomass could provide a solution for another problem, the need for sustainable energy. Instead of only producing 'clean' soil, biomass could be produced on the same area (double use). Nutrients from the sediment could stimulate the biomass production. The treatment time may require several years to decades and the produced soil may even reach the target values for multifunctional land use. Landfarming not only supports vegetation growth, but willows or other plants grown for biomass production will also stimulate the necessary processes for landfarming of sediments.

Landfarming for quality improvement during use. Depending on the initial concentrations of contaminants, soil reuse may be limited. However, as slow but continuous treatment occurs (possibly for decades), a clean soil may be produced for multifunctional societal purposes. An example is reuse of polluted soil or sediment as cover of a dike. The cover will become cleaner and risks also reduce during use. Other examples include using the soil or sediment to support vegetation in a noise wall or to cover a landfill.

Sustainable reuse of restored land for sustainable economic development. In the United States the development of the Environmental Protection Agency Brownfields Program under Superfund has targeted contaminated sites for economic development. These sites contain residual contamination that is considered to present an acceptable risk for limited uses. Utilising a parallel approach with landfarming for sustainable restoration of soil, it may be possible to utilise the restored land for economic development that would provide sustainable resources to repay the costs incurred by landfarming and to develop additional economic resources for the associated community or country. Examples include the sale of vegetation for energy, production and sale of compost as a soil conditioner, silviculture applications for furniture and electric power poles, and structures including domestic houses and businesses.

Landfarming for diffuse polluted sites. Many contaminated soils have contaminant concentrations slightly above levels for minimum risks. People often avoid areas containing these soils, and these soils are a problem in new developments. They are 'not dirty enough to be cleaned, but too dirty to be used for everything'. Landfarming, especially passive landfarming, is very appropriate for the sustainable restoration of soils and sediments in many world-wide situations where it is not currently being 'explored' for such use. Identifying the site soil assimilative properties provide the basis for extending the technology of landfarming beyond remediation to sustainable restoration. In addition, sustainable restoration of soil takes into account risk assessment and reduction, and management issues and criteria. The economic and social benefits that may accrue due to sustainable development of restored soil/land provide a technology where theories can be applied to specific situations, not only in The Netherlands, but world-wide.

Sustainable landfarming can be applied to large scale polluted sites, such as military sites, old industrial areas and oil exploration sites all over the world. Especially if more intensive cleaning technologies are too expensive for large scale pollution, sustainable treatment of the soil and area may be a solution.

Not all sediments in The Netherlands are polluted to such a degree that active bioremediation is necessary. Part of the sediment is clean and may be used for multifunctional uses after dredging. Another part, however, is also too dirty to be used for multifunctional uses but not dirty enough to be cleaned intensively. In practise this sediment is still spread out on adjacent land. Results of biodegradation on landfarms can support this practise. It is the question whether spreading influences the quality of the agricultural land after repeated dredging and spreading.

1.4.2 Heavy metals

Landfarming is an effective method for PAHs and mineral oil contaminated sediments. However not all contaminants are biodegradable. There are also sediments, in which a mixture of contaminants is present, and removal of the biodegradable contaminants does not mean that the remediated sediment is clean enough to be reused. Also the risk of persistent heavy metals present in the sediment should be considered. As long as the heavy metal contamination is low, the bioremediated soil can be applied as building material. Sediments with a large heavy metal concentration may cause a problem. To reach the target value it will be necessary to remove the heavy metals. Natural processes applicable in a landfarm to remove heavy metals are uptake by vegetation (phytoremediation) and leaching. Under natural conditions, these are both slow processes. Another way is reducing the risks by immobilisation of the heavy metals through the addition of binding substances or stimulating immobilisation processes.

Sediments treated on a landfarm should be selected to have a low content of heavy metals. However, on diffuse polluted sites, the presence of heavy metals can be of greater importance, such as when sediments are spread over agricultural land. Heavy metals in sediments are not the subject of this thesis, but ways of decreasing their risks in combination with landfarming are discussed in the evaluation.

1.5 Aim and scope of this thesis

The research described in this thesis is focussed on:

- Theoretical description of the landfarming process for bioremediation of PAHs and mineral polluted sediments. Giving a theoretical background to the rate of degradation in the short-term, but also in the long-term. Explaining the limiting factors during the bioremediation process on a landfarm.
- Study of the degradation of PAHs and mineral oil on a landfarm over 12 years, in order to differentiate between the initial fast degradation and the following slow degradation.
- Means of improving landfarming of sediments during the different phases of treatment, including increased temperature, improved aeration, and addition of degrading organisms.

- Establishment of environmental risks caused by the contaminants during treatment on the landfarm.
- Investigation of degradation of organic contaminants in both heavily polluted sediments on a landfarm and slightly polluted sediments that are spread on agricultural fields.

The results are used to support the concept of passive landfarming, in which as few as possible labour and energy input are used. Passive landfarming can be considered a sustainable technology that can even produce clean soil suitable for all uses in the long term. Theories and results are combined to predict the time necessary to reach a certain target or background value. Information provided in this thesis can be used to design a landfarm, but also to stimulate the biodegradation of PAHs and mineral oil in dredged sediment and in soils in more natural environments. For instance, passive landfarming and normal agricultural treatment of fields are closely related.

1.6 Outline of this thesis

This introduction described:
- The evolution of landfarming, from a pure clean-up technology to a method that can be used under more natural conditions
- Effect of regulations on the use of landfarming.
- Differentiation between intensive and passive ways of landfarming.

The introduction is followed by two theoretical chapters related to factors that influence the result of landfarming.

Chapter 2 Processes in a landfarm

Biodegradation of PAHs and mineral oil occurs if the contaminant is available to the micro-organisms and if oxygen is available to activate the degradation process. The availability of the contaminant is described using desorption processes and transport to sites in the sediment matrix where active micro-organisms are present. Because sediments are fully saturated with water and anaerobic, the dredged sediment has to be dewatered in order to achieve aeration. The physical processes relevant for aeration are described and used in a model to evaluate the different parameters.

Chapter 3 Chemical measures of bioavailability

Bioavailability of the contaminant is considered as the limiting factor for bioremediation. If it is possible to measure the bioavailability, it is also possible to predict the results of bioremediation or the (eco)toxicological effects of the contaminant. Starting with the concepts of bioavailability, chemical measurements are described that can be used to predict the fraction of the contaminant available for degradation

The two previous theoretical chapters are followed by five chapters based on experiments under field conditions and supported by laboratory experiments.

Chapter 4 Degradation and desorption of PAHs: kinetical approach

On the landfarm Kreekraksluizen located in the south-west of The Netherlands, sediments have been landfarmed since 1990. The extent of degradation and the degradation rate of PAHs have been measured and presented for degradation of available fractions. The rates are compared with desorption rates as measured with the TENAX-method, which is one of the measurements for bioavailability described in Chapter 3. The established rate coefficients are used to predict the result of landfarming.

Chapter 5 Degradation of mineral oil in landfarmed sediments

Mineral oil is one of the most common contaminants and was also present in the investigated sediments. Degradation rates of mineral oil in sediments are small compared to rates measured in contaminated soils, which is related to the different composition of the mineral oil in sediment. Degradation rates measured in sediments on the landfarm Kreekraksluizen are also presented as different for degradation available fractions.

Chapter 6 Effects of optimisation of landfarm treatment on the results of bioremediation

During the landfarm treatment of sediments on Kreekraksluizen, different methods are investigated to increase the degradation rate like increasing temperature and aeration, addition of fungi, and phytoremediation. The results are compared with the degradation in the ongoing landfarm.

Chapter 7 Environmental and ecological effects during landfarming of contaminated sediments

The effect of bioremediation can also be related to the reduction of risks. Environmental risks are leaching of contaminants and effects on organisms, which both have been measured. Using soil-protecting measures can diminish the first risk and the necessity of these measures is discussed. The risks for organisms are measured by bio-assays with water- and soil dwelling organisms and also by following ecological recuperation of the soil that occurs in the landfarm during treatment.

Chapter 8 Effect of spreading of slightly contaminated sediments on agricultural fields

In The Netherlands large amounts of slightly polluted sediments are spread over adjacent land. In fact this is a form of landfarming and degradation of PAHs in an agricultural system is described. The slow degradation rate may lead to accumulation; data on accumulation are presented together with calculated values based on the degradation rates presented in Chapter 4.

The previous chapters are evaluated in:

Chapter 9 Evaluation and discussion of landfarming of contaminated sediments

With slow degradation, a long period may be necessary to clean the soil or sediment. With a large amount of bioremediadable sediment and soil, too much space is required for remediation sites. This is not acceptable in a densely populated country as the Netherlands. Landfarming has to be combined with beneficial land use and applications of this way of landfarming will be discussed.

An evaluation is not complete if limiting factors are not considered. Unfortunately not all contaminants are biodegradable. PAHs and mineral oil can be present in combination with non-degradable heavy metals. Possibilities to reduce the risks of heavy metals in combination with landfarming will be discussed. This chapter presents an overview of the future use of landfarm technology in sustainable soil systems.

The thesis is summarised in the last chapter (***Summary***). The relation between the different subjects described before is given in Figure 1.3.

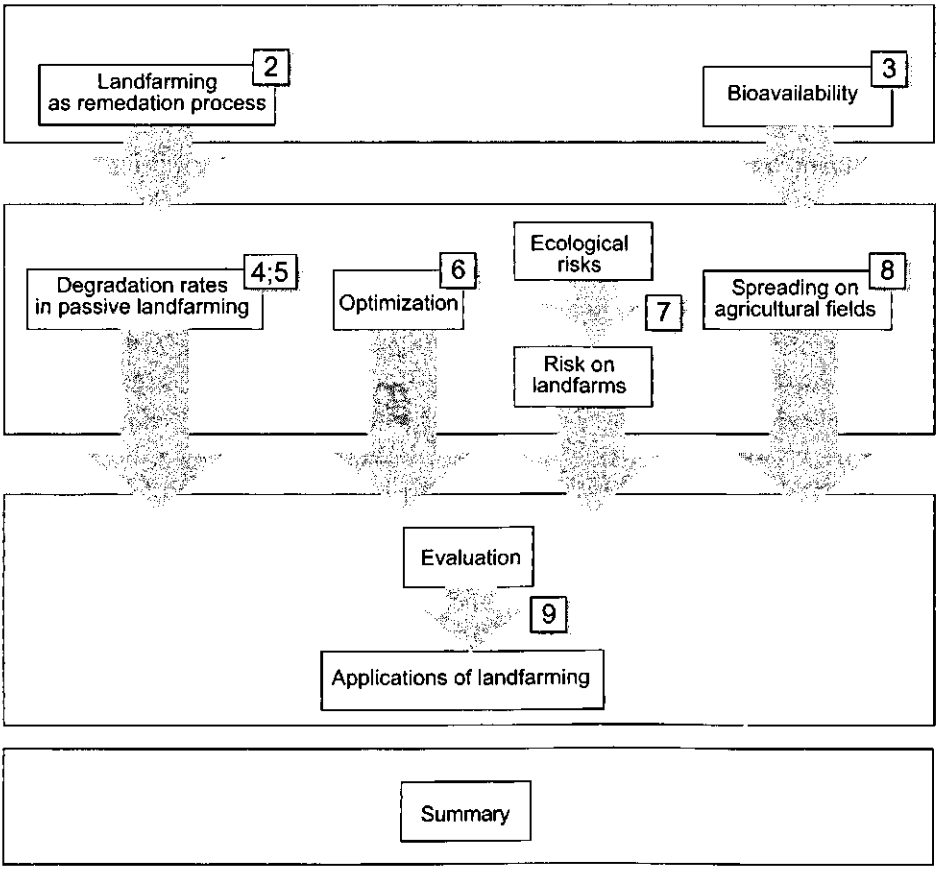

Figure 1.3 Scheme giving the relations between the different chapters. Numbers refer to the chapters in this thesis.

2 Processes in a landfarm

2.1 Introduction

Landfarming of dredged sediments starts with dewatering of the sediment that allows oxygen to enter the sediment through pores in which water is replaced by air. Under aerobic conditions biodegradation of contaminants like polycyclic aromatic hydrocarbons (PAHs) and mineral oil becomes possible. Aerobic biodegradation of contaminants in a landfarm will occur if the contaminant passes the cell membrane or enters the bio-influenced zone (see Chapter 3) of a micro-organism that is able to degrade the contaminant and if oxygen is present to initiate the biochemical reactions in the organism. Of coarse there may be other limiting conditions including too low or too high pH, lack of nutrients, or presence of chemicals inhibiting micro-organism activity. These conditions may make bioremediation either impossible to overcome or possible to manage, for example, by adding nutrients.

There are several concepts and mathematic formulations available to describe the fate of contaminants, the activity of micro-organisms and aeration in sediment. These can be applied to describe processes in a landfarm. This chapter is not an overview of all knowledge on these subjects. Knowledge is used to be able to recognise the most important parameters in landfarming of sediments. Most of the processes are also important in normal agricultural land use. Theories developed to describe the environmental impact of land use in rural regions (Rijtema *et al.*, 1999) have been applied to improve the understanding of processes in a landfarm. Subjects treated in this chapter include:

- Presence of contaminants in landfarmed sediment and, more specifically, the possibilities of transport of the contaminants to a site with an active micro-organism.
- Presence and activity of micro-organisms able to degrade PAHs and mineral oil.
- Presence of oxygen in sediment and soil and physical factors explaining the transport of oxygen. Sediments are anaerobic from origin and have to be changed into an aerobic soil. The oxygen supply should be sufficient over the whole layer of sediment applied.

Although the three subjects are discussed separately, they are of equal importance for landfarming. In order to achieve degradation, contaminant, oxygen and micro-organisms must be present at the same time and the same place. The result of a bioremediation process, i.e. the fraction of the contaminant degraded during a specified time, can be expressed as a summation of probabilities of each term or parameter (Harmsen *et al.*, 1997). The fraction degraded in a volume of sediment considered can be expressed as:

$$(\text{Fraction degraded})_t = \frac{\sum_{t}\sum_{x,y,z}\sum_{n_t}[\textit{contaminant}].[\textit{micro-organism}].[\textit{oxygen}]}{n_c} \qquad (2.1)$$

where:

[*contaminant*] = probability of finding the contaminant molecule on a site x,y,z per unit of time

[*micro-organism*] = probability of finding an active degrading micro-organism on site x,y,z per unit of time

[*oxygen*] = probability of finding oxygen on site x,y,z per unit of time

t = time elapsed after start of bioremediation in unit of time

x,y,z = co-ordinates in the volume considered

n_c = number of contaminant molecules in the volume considered

Each probability for *contaminant*, *micro-organism*, and *oxygen* terms can have the value zero or one; contaminant, micro-organisms and oxygen are present or not present. If the fraction degraded equals one it means that all the contaminant molecules have been biodegraded. The three probabilities are not all equal to one at he same time and at same position. For instance, starting with fresh sediment the probability of finding oxygen is zero and no biodegradation occurs, even if the probability of finding the contaminant and micro-organism are both 1. During dewatering the probability of finding oxygen increases and the probability of finding an active micro-organism becomes important. Active means that the micro-organism is able to degrade the contaminant present instantaneously. If the number of contaminant molecules at a certain site is too large for the micro-organism present, the probability of finding an active organism is not 1 and more micro-organisms or a longer time is necessary for degradation. Finally the contaminant molecules will not be present at sites with micro-organisms and oxygen; they are adsorbed in very small pores in the organic matrix. Diffusion to sites where degradation occurs is necessary. The probability of finding a contaminant on the proper site becomes important. Because there is also a summation over time, the limit of this equation (1 = all contaminants are fully biodegraded) will be reached, however, no indication of the time needed to reach a fraction degraded of one is included.

Equation 2.1 shows that it is useless to increase the probability of any specific term if this probability is already large and the probability of another term is much smaller. This equation can be considered as an overall model, however the input data for this model are not available. As a result, at this time the proposed model is a conceptual model that provides a framework and approach for the design, operation, and management of the landfarming process. The conceptual model (Equation 2.1) indicates that improvement of the result of landfarming will only occur if it is possible to improve the limiting process.

In this chapter the presence of contaminants, micro-organisms and oxygen in landfarmed sediment including mathematical formulations describing relevant processes, are discussed. The model and theories described in this chapter are not intended to give exact prediction of results of landfarming. They are used to evaluate the effect of changing specific parameters on the results of landfarming of sediments. They can be extended to predictive models, but in that case they have to be accompanied by appropriate input data (Vermeulen *et al.*, 2004). The model and theories have been made applicable for sediments treated on the landfarm Kreekraksluizen, also described in other chapters of this thesis (Petroleum Harbour and Wemeldinge sediment).

2.2 Presence of the contaminant

Interactions of contaminants with sediment and soil are often described using the equilibrium approach, which describes the partition between the aqueous and solid phases. As will be explained this approach is insufficient to describe the low organic chemical biodegradation rates in landfarms. Therefore the equilibrium approach is extended with a mathematical description of transport of the contaminant in soil aggregates, which introduces the time factor. Theories for transport in soil and distribution of the contaminant between the water phase and soil phase can be used for sediments, because the transport of contaminant becomes important after dewatering and during ripening. During this period sediment changes into soil. With this theory it becomes possible to predict the rate at which a contaminant becomes available for degradation.

Another approach is to address changes in the amount and type of organic matter, which is responsible for the adsorption of organic contaminants. Within short periods of time the organic matter in soil is a constant parameter. However, regarding the long treatment times as described in this thesis, organic matter will change in properties, can be degraded and also new organic matter (root residuals) will be built up. These changes and the rates of these changes can be used to explain biodegradation of contaminants.

2.2.1 Equilibrium approaches

Contaminant-soil interactions

PAHs are strongly adsorbed to the soil organic matter (*SOM*). In an equilibrium situation the adsorption of the contaminant can be expressed with a partition coefficient. The partition coefficient between organic matter and water is often expressed as K_{oc}. In this constant organic matter is expressed as organic carbon. Adsorption, as an equilibrium process, can be considered as the presence of a contaminant on the surface of a soil particle or the surface of a soil pore, at a concentration that is in equilibrium with the concentration in the mobile pore water. Mobile pore water takes part in transport processes and is present in the larger pores. The presence of a contaminant within the organic matter is called absorption and absorbed contaminants are in general not in equilibrium with the mobile pore water due to the lack of direct contact. In this chapter absorption of contaminants as a major process affecting landfarming will be discussed further.

Experimental data on adsorption of different organic contaminants in soils and sediments were collected and generalised in such a way that in many cases predictions can be made with respect to the equilibrium sorptive behaviour of contaminants of which only a few physical-chemical parameters, such as the octanol/water partition coefficient K_{ow} and the water solubility S, are known (Briggs 1973, Karickhoff *et al.*, 1979, Friesel 1987, Lagas and Hammers 1987). Kooper *et al.*, (1987) presented the following relations based on data collected from literature for 127 organic compounds:

$$\log K_{oc} = 0.989 \log K_{ow} - 0.346 \tag{2.2}$$

and

$$\log K_{oc} = -0.729 \log S + 0.231 \tag{2.3}$$

where:

K_{oc} = partition coefficient between organic matter (expressed as organic carbon) and water

K_{ow} = octanol/water partition coefficient

S = water solubility in mole/dm^3

Other authors have presented similar equations (Means *et al.*, 1980; Gawlik *et al.*, 1997; Seth *et al.*, 1999 and Xia and Pignatello, 2001). Cuypers (2001) stated that in literature presented K_{oc} values exhibit considerable variation from sorbent to sorbent. They may vary by a factor 1-3 in magnitude. For the evaluation of the risks of PAHs, Otte *et al.*, (2001) have evaluated the K_{ow} and K_{oc} values. The measurement of partition coefficients was not and objective of this study and the K_{oc} values’ presented by Otte *et al.*, (2001) are used and presented in Table 2.1. Remarkable in this series are the high log K_{ow} values for dibenzo[a,h]anthracene and indeno[1,2,3-c,d]pyrene. Other properties of PAHs used in this chapter are also presented in Table 2.1, as there is the absorption to dissolved organic matter (*DOM*) that can be described with a partition coefficient value similar to that described by Equation 2.2. The presented values are calculated, as described further (Equation 2.6). Other presented properties are the molar mass (*M*), the solubility (*S*) and the diffusion coefficient in water (D^w).

Table 2.1 Properties of PAHs. PAHs that are investigated in this study are printed bold.

PAH	Abbreviation used	*M*	$-\log S$	$\log K_{ow}$ 1)	$\log K_{oc}$ *SOM* 1)	$\log K_{oc}$ *DOM* 2)	D^w
		g/mole	S in mole/dm^3				10^{-4} m^2/d
Naphthalene		128	3.62	3.30	2.98	2.92	1.40 4)
Acenaphthylene		152	4.59	3,94	3.47	3.69	1.32 4)
Acenaphthene		154	4.61	3.92	3.53	3.67	1.32 4)
Fluorene	FLU	166	4.94	4.18	3.77	3.98	1.29 4)
Phenanthrene	PHE	178	5.21	4.47	4.23	4.33	1.22 3)
Anthracene	ANT	178	6.60	4.45	4.30	4.30	1.23 3)
Fluoranthene	FLT	202	5.89	5.16	5.18	5.16	1.17 3)
Pyrene	PYR	202	6.19	4.99	4.83	4.95	1.16 3)
Benz[a]anthracene	BaA	228	7.32	5.54	5.79	5.61	1.06 3)
Chrysene	CHR	228	8.06	5.81	5.72	5.94	1.06 3)
Benz[b]fluoranthene	BbF	252	7.32	5.78	5.34	5.90	1.08 4)
Benz[k]fluoranthene	BkF	252	8.66	6.11	6.24	6.30	1.04 4)
Benz[a]pyrene	BaP	252	7.82	6.13	5.82	6.32	1.04 4)
Dibenzo[a,h]anthracene		278	8.67	7.11	6.14	7.50	0.91 4)
Benzo[g,h,i]perylene	BPE	276	9.03	6.22	6.43	6.43	1.03 4)
Indeno[1,2,3-c,d]pyrene	IPY	276	6.65	6.87	6.02	7.21	0.95 4)

1) Otte *et al*, 2001

2) Calculated according Equation 2.6

3) Bonten, 2001;

4) Estimated by extrapolation, assuming a linear relation between log K_{ow} and D^w given as:

$$10^4 D^w = -0.128 \log K_{ow} + 1.824$$

From an analytical point of view, the amount of carbon present in organic matter is a good estimate for organic matter content in soil and sediment and is therefore used in the K_{oc}-value. Organic matter is the real constituent of soil and sediment and in the calculations it is assumed that 1 g organic matter contains 0.58 g organic carbon. In modelling the linear partition coefficient between soil and water (K_d) is often used, because this includes the concentration in both the pore water and the solid phase.

$$K_d = 1000\, fr_{oc}\, K_{oc} = 580\, fr_{om}\, K_{oc} \tag{2.4}$$

where;

K_d = linear adsorption coefficient in m³/kg

fr_{oc} = mass fraction of organic carbon in kg/kg

fr_{om} = mass fraction of organic matter in kg/kg

Equation 2.4 is valid if PAHs only interact with soil organic matter. There is, however, also an interaction with dissolved organic matter (*DOM*) (Comans *et al.*, 2000), which is stronger for the highly insoluble PAHs. *DOM* is mostly expressed as dissolved organic carbon (*DOC*). Also the interaction of the contaminant with *DOC* can be described with a partition coefficient between dissolved organic carbon and water: K_{oc}^{DOC}. In the expression for K_d the amount in the water phase has to be replaced by the sum of the free dissolved PAHs and the PAHs associated with the solved organic matter.

$$K_d = \frac{1000\, fr_{oc}\, K_{oc}}{[1 + fr_{DOC} K_{oc}^{DOC}]} \tag{2.5}$$

where:

fr_{DOC} = mass fraction of organic carbon dissolved in water in kg/kg

K_{oc}^{DOC} = partition coefficient between dissolved organic matter (expressed as organic carbon) and water

K_{oc}^{DOC} can be described similar as the K_{oc} for solid organic matter *SOM*, using data from literature (Lüers and Ten Hulcher, 1996; Poerschman and Kopinke, 2001; Mackay and Gschwend, 2001 and Laor and Rebhun, 2002) as presented in Figure 2.1. Reported values differ by a factor up to 6. The correlation can be described with:

$$\log K_{oc}^{DOC} = 1.20 \log K_{ow} - 1.04 \quad R^2 = 0.88 \tag{2.6}$$

where:

R = correlation coefficient

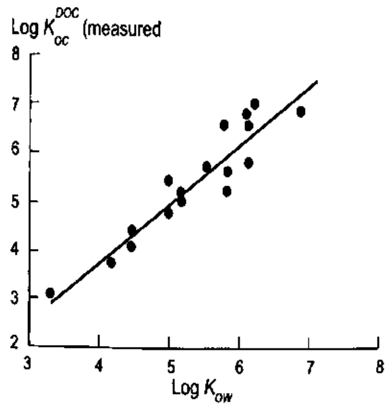

Figure 2.1 Relation between measured K_{oc}^{DOC} (values from literature) and the K_{ow} value (Table 2.1).

Reinds *et al.*, (1995) showed for forest soils, with organic matter contents between 0.2 and 10 %, that *DOC* in water, expressed in kg/m³ can be approximated by:

$$\log DOC = 0.611 + 0.38 \log fr_{om} \tag{2.7}$$

Vermeulen and Hendriks (1996) gave a maximum value of *DOC* of 0.12 kg/m³ and Van Breemen *et al.*, (1988) report concentrations up to 0.14 kg/m³. *DOC* values measured in the drainage water of the landfarms on Kreekraksluizen are between 0.05 and 0.10 kg/m³. The presence of dissolved organic matter in the water phase results in a smaller range in the K_d values at higher *DOC* values as shown in Figure 2.2. Mackay and Gswhwend (2001) have reported increase of the solubility of PAHs at a coal tar site which are in agreement with these calculations. The importance of dissolved organic matter for the increase of the solubility of PAHs is also shown by Holman, (2002). Using infrared microscopy and a very bright, non-destructive synchrotron photon source, the authors showed that in presence of organic matter (humic acids) bacteria could degrade pyrene faster than in absence of organic matter.

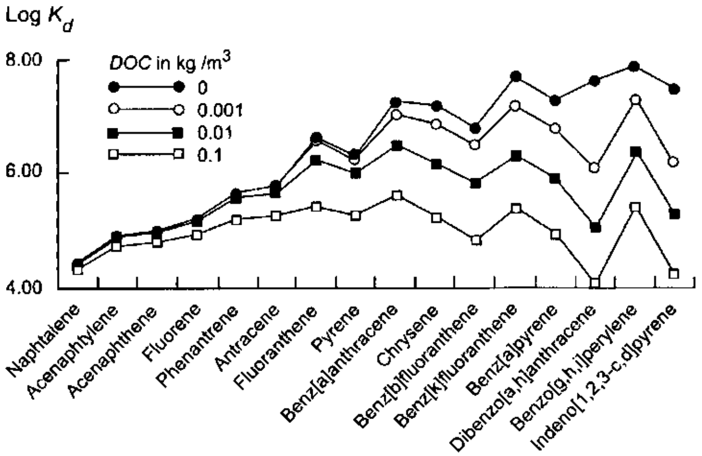

Figure 2.2 The effect of dissolved organic matter (*DOC* in kg/m^3) on the calculated distribution coefficient Kd of PAHs in soil (m^3/kg). Fraction organic matter in sediment 0.05 kg/kg.

2.2.2 Non-equilibrium sorption

Mathematical description of the rate constant

Application of the equilibrium approach has not worked well in several situations, most notably for strongly adsorbed contaminants like many organic chemicals. The adsorption and desorption rate can be limited by internal diffusion processes, which control the transfer of compounds from the interior of the adsorbent to the external surfaces and opposite. If internal diffusion processes are rate limiting an adsorption model based on Fick's second diffusion law can be utilized to describe the process. A number of chemical-kinetic and diffusion controlled models have been proposed in the literature to describe non-equilibrium sorption, varying from relatively simple first order kinetic rate equations, multi-compartment sorption, to two region transport involving contaminant exchange between mobile and relatively immobile liquid regions. Van Genuchten and Šimůnek (1996) give an extended discussion of the different time dependent formulations that can be used, taking into account the geometry of the adsorption sites.

Not considering the shape of the sediment/soil particle or aggregate (linear), and assuming a physically controlled first-order kinetic rate process and equilibrium between the sorbed amount and pore water, the simplest one-site non-equilibrium formulation is obtained (Rolston *et al.*, 2003):

$$\frac{\partial c}{\partial t} = k \, . \, c \qquad (2.8)$$

where:

k = first order kinetic rate constant in d^{-1}

c = contaminant concentration in the aggregate in kg/m^3

and the integrated form for *c* as a function of time is:

$$\frac{c_t}{c_0} = e^{-k \cdot t} \qquad (2.9)$$

in which:

c_o = sorbed concentration at $t=0$

c_t = sorbed concentration at $t=t$

The rate constant in this equation has to be considered as an empirical rate constant. It includes physical factors like the shape of the soil aggregate and the moisture content. In the field degradation studies and desorption studies presented in following chapters, the experimental established rate constant are also empirical. In order to explain differences it is necessary to know which specific physical factors are included in the rate constant. For a structured soil, which is the result of landfarming sediment, the first order transport process can be modelled more realistically. The transport of a contaminant in a single aggregate, containing pores that are partially filled with water as illustrated in Figure 2.3, has been described by a general diffusion equation by Rijtema *et al.* (1999). They included the shape of the aggregate (sphere, cylinder or plate) by the shape factor *m*. The diffusion equation can be solved numerically, which result an equation like 2.9, in which the rate constant *k* is expressed as:

$$k = \frac{2(m+1)\, D_s^w}{[\theta + \rho_s (1-\varepsilon) K_d] r^2} \qquad (2.10)$$

where:

θ = internal aggregate moisture content in m^3/m^3

ε = volume fraction of total pore space in the aggregate (water and air filled) in m^3/m^3

r = distance from the surface to the centre of the aggregates in m

m = shape factor for the aggregate structure ,with
m = 0 for plate aggregate;
m = 1 for cylindrical aggregate;
m = 2 for spherical aggregate
ρ_s = specific weight of the soil in kg/m^3
D_s^w = contaminant diffusion coefficient in sediment/soil pore water in m^2/d

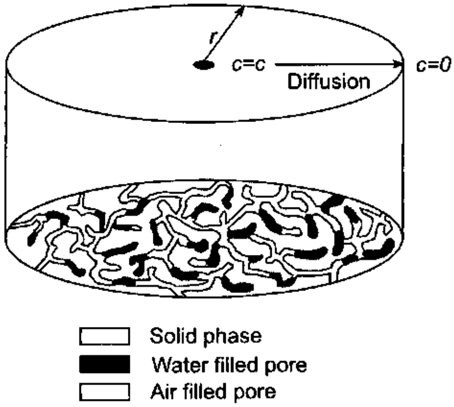

Figure 2.3 Transport of a contaminant in a single aggregate.

The internal aggregate moisture content θ has to be considered in unsaturated soils as the immobile moisture fraction and depends on clay content and organic matter content. In aerobic unsaturated soils, its value varies from 0.02 in sandy soils with very low organic matter content to about 0.50 in soils rich in clay and a high content of organic matter. In sediments the moisture content will be much higher and reach values of 0.7.

The contaminant diffusion coefficient in soil pore water D_s^w is still an unknown and can be approximated through the introduction of a tortuosity factor η (Equation 2.11). D^w is the contaminant diffusion coefficient in water in m^2/d.

$$D_s^w = \eta \, \theta \, D^w \qquad (2.11)$$

The value of η depends on the clay and moisture content as shown in Equation 2.12 (Rijtema *et al.*, 1999)

$$\eta = -0.00389 \, fr_{cl} + 1.28 \, \theta \qquad (2.12)$$

where:

fr_{cl} = weight fraction of clay

Using the values of D^w given in Table 2.1, the values of D_s^w can be calculated. However, the dissolved organic matter also influences the diffusion coefficient. The associated molecule is much larger and will consequently diffuse more slowly than the individual PAH molecule. The diffusion coefficient of the associated *DOM*-PAH molecule can be estimated using the expression (Trapp and Matthies, 1997):

$$D^w(DOM\text{-PAH}) = 1.728 \cdot 10^{-4} \cdot \sqrt{(32/M)} \tag{2.13}$$

where:

M = molar mass

The effect of temperature on the diffusion coefficient of PAHs is low with approximately a 20% increase for every 10 °C temperature increase (Bonten, 2001), which shows that elevating the temperature to reduce the residual concentration is not very effective if diffusion is limiting for degradation. Values of the diffusion coefficient for phenanthrene are presented in Table 2.2 together with values for oxygen. Oxygen behaviour in a landfarm is further described in Section 2.4. An increase in temperature will increase the diffusion coefficient for oxygen slightly more than for phenanthrene.

Table 2.2 Relation between temperature and the diffusion coefficient of phenanthrene and oxygen in water.

Temperature	Diffusion coefficient (m^2/d)	
(°C)	Phenanthrene[1)]	Oxygen[2)]
5		$1.10\ 10^{-4}$
10		$1.33\ 10^{-4}$
15		$1.57\ 10^{-4}$
20	$0.71\ 10^{-4}$	$1.81\ 10^{-4}$
25		$2.06\ 10^{-4}$
30	$0.92\ 10^{-4}$	$2.31\ 10^{-4}$
40	$1.17\ 10^{-4}$	

1) Bonten, 2001; 2) Rijtema *et al.*, 1999

The specific weight of the soil ρ_s in Equation 2.11 depends on the clay-, sand- and organic matter fraction (respectively fr_{cl}, fr_{sa} and fr_{om}) and their densities (respectively ρ_{cl}, ρ_{sa} and ρ_{om}) and can be calculated as:

$$\rho_s = fr_{cl}\,\rho_{cl} + fr_{sa}\,\rho_{sa} + fr_{om}\,\rho_{om} \tag{2.14}$$

Using the relations for D_s^w (Equation 2.11) and η (Equation 2.12), and limiting the application to components with high K_d values, the expression for the rate constant as given in Equation 2.10 can be simplified as:

$$k \sim \frac{\theta^2}{(1-\varepsilon)r^2} \tag{2.15}$$

Because the moisture fraction is a variable, this equation can be used in comparing unsaturated situations (landfarm) and saturated situations as present in laboratory desorption studies (Chapter 4). The simplification is not valid in situations with high clay content and low moisture content, which only occurs under extreme dry conditions.

Calculation of the rate constant

Because all constants in the expression for the rate constant k (Equation 2.10) now have a physical meaning, it is possible to calculate this constant for a specific situation and to evaluate the influence of several parameters on the rate constant. In Table 2.3 the effect of the association of PAHs with dissolved organic matter is presented. Column one shows the effect of ignoring the interaction of the PAH with *DOM*. In column two K_D is corrected for the interaction with *DOM* (Equation 2.5), and column three shows the effect of introducing a proper diffusion coefficient for the associated molecule with an assumed molecular weight of 2000 (Trapp and Matthies, 1997) while retaining interaction with *DOM*. Other values used are:

- The radius of the cylindrical aggregate $r = 10^{-5}$ m.
- Aggregate moisture content $\theta = 0.50$ m^3/m^3.
- Total pore space $\varepsilon = 0.55$ m^3/m^3.
- Fraction organic matter $fr_{om} = 0.05$ kg/kg.
- Fraction clay $fr_{cl} = 0.1$ kg/kg.
- Specific weight clay $\varrho_{cl} = 2700$ kg.m^{-3}; specific weight sand $\varrho_{sa} = 2650$ kg/m^3 specific weight organic material $\varrho_{om} = 1400$ kg/m^3.
- Dissolved organic carbon $fr_{DOC} = 10^{-4}$ kg/dm^3.
- K_{oc} *(SOM)* and K_{oc} *(DOM)* as given in Table 2.1.

Without the interaction with *DOM*, the variation in calculated rate constant k is large (second column of Table 2.3). Including *DOM* (third column) brings the values together. As result of the higher K_{ow} values for dibenzo[a,h]anthracene and indeno[1,2,3-c,d]pyrene (Table 2.1) the calculated values for these PAHs are also larger. Including the diffusion coefficient makes the relative differences between the calculated values smaller. As shown with measured data in Chapter 4 (Table 4.4 and

4.5) it is necessary to include the *DOM*-PAH interaction. Without including this interaction the range in calculated values is too large. In the last column also the diffusion coefficient of the associated *DOM*-PAH molecule is taken into account, which decreases the *k*-values and brings them also more together.

Table 2.3 Calculated rate coefficients for desorption in a soil aggregate. *DOC*=100 mg/l; r = 10^{-5} m, other constants see text above.

PAHs	Calculated *k*-values (y^{-1})		
	No interaction with *DOM*	*Kd* corrected for *DOM*	Diffusion coefficient for *M*=2000
Naphthalene	20	22	3.43
Acenaphtylene	6.1	9.2	1.52
Acenaphthene	5.2	7.9	1.31
Fluorene	3.0	5.9	1.00
Phenanthrene	0.99	3.1	0.56
Anthracene	0.85	2.6	0.45
Fluoranthene	0.11	1.7	0.31
Pyrene	0.24	2.4	0.44
Benz[a]anthracene	0.024	1.0	0.20
Chrysene	0.028	2.5	0.51
Benz[b]fluoranthene	0.062	5.5	1.11
Benz[k]fluoranthene	0.008	1.7	0.35
Benz[a]pyrene	0.022	4.6	0.96
Dibenzo[a,h]anthracene	0.010	29	6.92
Benzo[g,h,i]perylene	0.005	1.4	0.30
Indeno[1,2,3-c,d]pyrene	0.011	20	4.68

Because there is a quadratic relation between the moisture content and the rate constant, the moisture content is a very important parameter as shown in Figure 2.4 for the desorption rate constants of some PAHs. Under saturated conditions (high moisture content) the highest rate constants are obtained. Desorption will be slower under more dry (unsaturated) conditions that are present in a landfarm during summer (Dutch climate).

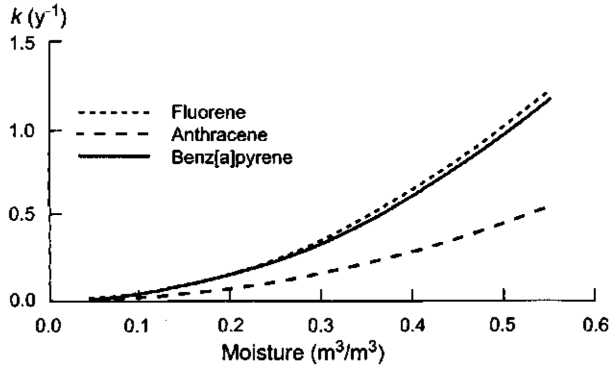

Figure 2.4 The effect of the moisture content on the calculated desorption rate constant of PAHs in sediments/soils. Constants used as in previous example.

The effect of the aggregate radius on the rate coefficient is presented in Table 2.4. The same parameters as in previous example are used, including the diffusion coefficient D_s^w of the *DOM*-PAH molecule with a molecular weight of 2000. Two extreme situations can be present:

- Desorption can be considered as instantaneous if the rate constant is large compared with the treatment time. In a landfarm the minimum treatment time is 3 months, and then *k*-values larger than 20 y^{-1} can be considered as instantaneously (bold values).
- If the *k*-value is very low, the material is immobile and has to be removed from the soil through decomposition of the organic material present in the soil (bold and italic values).

Table 2.4 Calculated rate constant k for different aggregate radii. Soil properties and other used constants see text above.

PAHs	Rate coefficient k in y^{-1}			
	$r = 10^{-6}$ (m)	$r = 10^{-5}$ (m)	$r = 10^{-4}$ (m)	$r = 10^{-3}$ (m)
Naphthalene	**343**	3.43	***0.034***	***0.00034***
Acenaphtylene	**152**	1.52	***0.015***	***0.00015***
Acenaphthene	**131**	1.31	***0.013***	***0.00013***
Fluorene	**100**	1.00	***0.010***	***0.00010***
Phenanthrene	**56**	0.56	***0.006***	***0.00006***
Anthracene	**45**	0.45	***0.005***	***0.00005***
Fluoranthene	**31**	0.31	***0.003***	***0.00003***
Pyrene	**44**	0.44	***0.004***	***0.00004***
Benz[a]anthracene	**20**	0.20	***0.002***	***0.00002***
Chrysene	**51**	0.51	***0.005***	***0.00005***
Benz[b]fluoranthene	**111**	1.11	***0.011***	***0.00011***
Benz[k]fluoranthene	**35**	0.35	***0.003***	***0.00003***
Benz[a]pyrene	**96**	0.96	***0.010***	***0.00010***
Dibenzo[a,h]anthracene	**692**	6.92	***0.069***	***0.00069***
Benzo[g,h,i]perylene	**30**	0.30	***0.003***	***0.00003***
Indeno[1,2,3-c,d]pyrene	**468**	4.68	***0.047***	***0.00047***

Instantaneous desorption occurs from soil particles < 10^{-5} m and desorption has to be considered as immobile in particles >10^{-3} m. In principle it is not the radius, but the distance between a contaminant and a micro-organism, but also in that case the values are realistic. This is within the range of particles and soil aggregates present in most soils and shows that the calculations can be used for prediction of the desorption rate.

Cultivation in a landfarm will reduce the particle size to a certain limit. Depending on the soil type (sand, peat or clay), mechanical reductions of the aggregate size to several mm can be achieved, which is not far enough to change a slow process into a fast process (see Table 2.4). To do this, greater size reduction is required. Technological this is possible in slurry reactors, but not in a landfarm. In a landfarm, natural processes like root activity and activity of worms can be responsible for a larger size reduction. It will be clear that it will take a long time before every soil particle is passed though a worm or has been penetrated by a root. However, there will be a positive effect of these activities on the desorption rate.

For bioremediation of polluted sediment an expensive slurry reactor or a cheap landfarm system can be used. For example in a slurry reactor fresh sediment will have a large pore volume, which is completely filled with water (both ε and θ can be about 0.7. In a landfarm the amount of moisture has to be much lower in order to have an adequate supply of oxygen. By dewatering and ripening also the pore volume reduces. Using a pore filled fraction of 0.55 and a moisture fraction of 0.35 gives a difference in the rate coefficient of a factor 6. Moreover, in a slurry reactor, aggregates are free floating and can even be reduced in size. The effective radius of soil aggregates in a slurry will therefore be smaller compared to the radius in a landfarm. A factor of two in size will already give a factor of four in the rate coefficient. Together this is a factor of 24 and sediment that can be cleaned in weeks in a slurry reactor, will require years in a landfarm. This will also be illustrated with measured values in Chapter 4. The theoretical approach described above also shows that fast and slow treatment rates correspond with respectively expensive and cheap technologies.

The highest desorption rates will be achieved in a saturated soil. This is not an option in a landfarm, because this will result in the oxygen supply becoming a limiting process for treatment (see also 2.4). There must be a high amount of gas filled pores, especially if thick layers have to be landfarmed. Moisture changes, wet periods followed by dry periods, in the short term (weeks) have not been shown to increase the degradation rate in the landfarming of pentachlorophenol (Harmsen 1993). Under all moisture conditions the same results were obtained, providing that aerobic periods were present. Long term changes have not been investigated, however the Dutch conditions, of wet weather during winter and dry during summer, may be satisfactory.

This type of modelling is very useful in understanding processes occurring in a landfarm. It should, however, be realised that a real prediction of the rate of degradation is still difficult. Several constants are not accurately known at this time. As identified before, the K_{oc} values for *DOM* and *DOC* may differ with a factor of, respectively, 3 to 6. The molar mass of *DOC* is not a specific value but a range and will differ from soil type to soil type. In a slurry reactor it may be possible to give a good estimate of the radius of soil particles present. In a landfarm in which an unsaturated soil is present it is difficult to make a good estimate of the radius of individual aggregates or the distance from an adsorbed contaminant molecule to an active micro-organism. In spite of these inaccuracies, the model is a proper tool to show the relative influence of the individual parameters.

2.2.3 Influence of adsorption sites

Multi-compartment model

The diffusion model described above considers a sediment/soil with constant properties of all adsorption sites (one compartment model). The resulting one-compartment first order kinetic model, gives generally poor results, because soil is a heterogeneous material. In general soil consists of many types of aggregates and within aggregates properties also differ. To take into account these differences, all the adsorption sites are divided into several compartments, of which the sorption to the first compartment is assumed to be instantaneously in equilibrium with the mobile pore water concentration and can be biodegraded.

Two compartment models have often been described (Brusseau *et al.*, 1991, Cornelissen *et al.*, 1997). In this study three desorbing compartments are distinguished. If desorption is the explaining factor for biodegradation, this model can also be used for degradation. Assuming that no re-adsorption takes place (Cornelissen *et al.*, 1997) the three-compartment desorption model can be described as sum of three first order decreases:

$$\frac{c_t}{c_0} = F_{fast} \cdot e^{-k_{fast} \cdot t} + F_{slow} \cdot e^{-k_{slow} \cdot t} + F_{very\,slow} \cdot e^{-k_{very\,slow} \cdot t} \qquad (2.16)$$

where:

c_t = sediment/soil sorbed amount (mg/kg d.m.) at time t (y)

c_0 = sediment/soil sorbed amount (mg/kg d.m.) at time 0

F_{fast} = fraction of contaminant in fast desorbing/degrading compartment

F_{slow} = fraction of contaminant in slow desorbing/degrading compartment

$F_{very\,slow}$ = fraction of contaminant in very slow desorbing/degrading compartment

k_{fast} = rate constant rapid desorption/degradation (y^{-1})

k_{slow} = rate constant slow desorption/degradation (y^{-1})

$k_{very\,slow}$ = rate constant very slow desorption/degradation (y^{-1}).

Every first order decrease is described with two constants, the size (fraction of total amount, F) and the rate constant (k). If degradation is not possible redistribution between the different compartments takes place, which may result in decrease of the fast desorbing fraction and increase of the slow and very slow desorbing fractions. This stronger binding of contaminants to sediment or soil as effect of increasing contact time is often described as aging.

Instead of a rate constant (k), half-life time ($t_{1/2}$) is often used as a characteristic value in a first order process. Table 2.5 gives half-life times and the corresponding k-values. In this thesis the dimension y^{-1} is used because it is close to the observed time scale. Publications on desorption kinetics often use the dimension h^{-1}, and the corresponding values with this dimension are therefore also presented. In the fourth column of Table 2.5 the time necessary to reduce the compartment to 90% of its original size is given. In the last column, examples are given of the bioremediation methods that can be used within the given time frame.

Table 2.5 First order decrease expressed as half life time (t½), rate constant (k), time necessary to have 90% reduction of a compartment and examples of bioremediation methods.

Half life time $t_{½}$	Rate constant k		Time needed for 90% reduction (y)	Example of bioremediation method
	(y^{-1})	(h^{-1})		
1 hour	6070	0.69	0.00038	
1 day	253	2.9×10^{-2}	0.0091	
1 week	36	4.1×10^{-3}	0.064	Bioreactor
1 month	8.4	9.6×10^{-4}	0.27	
1 year	0.69	7.9×10^{-5}	3.3	Intensive landfarm
5 years	0.14	1.6×10^{-5}	17	
10 years	0.069	7.9×10^{-6}	33	Passive landfarm
20 years	0.035	3.9×10^{-6}	66	Natural attenuation

The assumption that no re-adsorption takes place will be true in slurry systems with a high biological activity or in experimental systems were the desorbed contaminant is immediately taken away. In both cases the concentrations in the water phase are zero. Examples are a bioreactor or the Tenax desorption test as described in Chapter 3 and 4. Fitting experimental data with a two or three compartment model will give desorption or degradation rate constants. In a landfarm the desorbed contaminant is not always taken away instantaneously. Limiting factors can be the absence of oxygen or an active degrading organism. As shown in Section 2.4 and 2.5, the duration of the period in which degradation is limited by absence of oxygen may vary. At the surface of the landfarm oxygen is present very quickly. However, with thicker layers more time is necessary to have the whole layer aerated. If oxygen is absent, desorption will not lead to degradation and re-adsorption will take place. As long as the fast desorbing fraction is still large, desorption and re-adsorption will lead to growing of the slow desorbing fraction (aging). The same is true when the slow and very slow desorbing fractions are compared.

Because of the long duration of the dewatering phase in our experiments, above considerations are not theoretical problems but reality. Fitting data in such a case with a two or three compartment model will not give proper degradation constants. The calculated degradation rate constant will be the result of both dewatering and degradation.

Organic matter

If all the different adsorption sites in organic matter are at random distributed, the net observed result will not be a summation of three first order decreases, but only one first order decrease with an 'averaged' rate constant. Different rates as in the multi compartment model imply clustering of different adsorption sites on larger scale. The multi compartment model can be given a physical background by introducing the ideas on different types of organic matter. (Weber *et al.*, 1992 and Pignatello and Xing, 1996), visualised in Figure 2.5. In this approach desorption from the organic matter is still the rate-defining step. Similar to polymers, organic matter can be distributed into two phases: an expanded phase and a condensed phase. The expanded phase is a rubber like phase, also called amorph phase (Luthy *et al.*, 1997). Sorption is linear, the diffusion coefficient does not depend on the concentration and there is no hysteresis. The condensed phase is a glassy phase, sorption is non linear, the diffusion coefficient depends on concentration and hysteresis occurs. The strong binding between organic matter molecules is responsible for a strong matrix (Pignatello, 1998). In this matrix adsorption occurs in internal micro-pores or voids of several nanometres. To reach or leave these pores diffusion through the condensed organic matter is necessary, which makes it a very slow process, much slower than desorption from the expanded phase. In addition to this the sorption capacity of older (condensed) organic matter is larger than the adsorption capacity of young organic matter (Johnson *et al.*, 2001). Cuypers (2001) showed experimentally that it is realistic to make distinction between expanded and condensed organic matter.

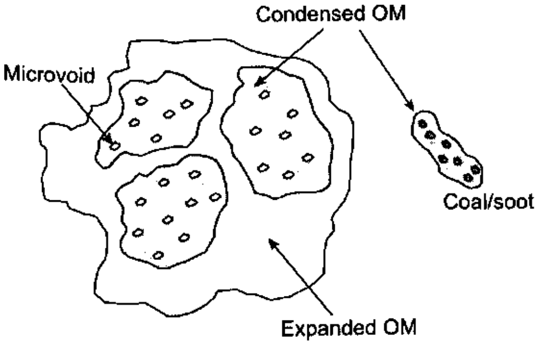

Figure 2.5 Schematic representation of organic material in soil/sediment (Cuypers, 2001).

The expanded and condensed phase may change into each other. In time, more condensed phase will be formed (Pignatello, 1998). Opposite it is more difficult, because the condensed phase is the more stable one and will not return to the less stable expanded phase. Transfer to the less stable expanded phase will not occur in a solid aggregate under normal conditions. Heating of soil (Bonten, 2001) or affecting the soil structure using high amount of sodium (De Jonge, 1996) can affect the amount of condensed organic matter. These actions are, however, not realistic in a landfarm and therefore not further discussed. The expanded phase is also subject of microbiological degradation and on the long-term also condensed organic matter will be microbiological degraded as described in next section.

Within this theory a residual concentration may still exist, that is not or very slowly degradable, which will be observed if organic matter in sediments also originate from contamination. Examples are tar, soot or black carbon and oil. PAHs can be adsorbed or absorbed by this non natural organic matter. This material can be considered as a special form of condensed organic matter. Presence of soot increases the strength of adsorption (Gustafson *et al.*, 1997; Accardi-Dey and Gschwend, 2001; Jonker and Koelmans, 2002; Cornelissen and Gustafson, 2004) Mineral oil can both reduce (competition) and increase (separate phase) the strength of adsorption (Jonker *et al.*, 2003). The desorption process in these particles is still based on diffusion, but it will be clear that diffusion in for instance a tar particle will be very slowly.

Decomposition of organic matter

Organic matter may change in composition as described above, which does not change the organic matter content and also decompose to give a lower organic matter content. Depending on the source, decomposition can be noticeable within a year or several decades. As also presented in Chapter 4, the organic matter in sediment from which desorption takes place is not constant. Especially in the first year of a landfarm, there is a large decrease of the organic matter due to degradation. As a result, desorption and diffusion to a site with an active micro-organism is not the only reason for degradation. PAHs also degrade because of the disappearance of the sorption site, which makes them available for degradation.

Organic matter can also be partly decomposed with the result that the availability of the contaminant increases, resulting in higher desorption rates of PAHs in this part of the organic matter. It is also possible that the decomposition leads to closing of small pores and smaller desorption rate constants for the PAHs. Comparable with desorption, decomposition can also be described with a first order decrease. Using a five-compartment model Rijtema *et al.* (1999) could describe the decomposition of organic matter for several types of organic matter in soil. Degradation rate constants for organic matter (k_{om}) were set and the fractions belonging to these rate constants were calculated from the degradation curves and presented in Table 2.5. It should be noticed that rates for complete decomposition are given. On a time scale of years and decades it is not possible to distinguish between desorption and decomposition of organic matter as the responsible process for biodegradation, because desorption as well as degradation of organic matter can be described with a sum of first order decreases.

Table 2.5 Fractions of different organic materials having specified degradation rate constant at an average soil temperature of 10 °C (Rijtema et al., 1999).

Organic material	Degradation rate constant k_{om} in (y^{-1}) and fractions (%)				
	2.15	**0.8**	**0.25**	**0.02**	**0.005**
Foliage	70	21	6	2	1
Straw	52	30	11	5	2
Litter deciduous trees	20	36	30	10	3
Farmyard manure	19	37	26	13	5
Sewage sludge	58	26	10	4	2
Compost	3	27	37	23	10
Peat 1	2	23	39	26	10
Peat 2	0	8	38	37	16
Peat 3	0	3	29	47	21
Peat 4	0	0	10	60	30

For biodegradation of organic matter, oxygen is necessary. Under complete aerobic conditions, the oxygen demand can be calculated, considering a carbon content fr_C in the sediment. Following Rijtema *et al.,* (1999), assuming complete oxidation of the organic material (based on glucose $C_6H_{12}O_6$) to CO_2 results in the fact that for the oxidation of each mole of C, 1 mole of O_2 is needed, yielding:

$$S_{ox}^{C} = \frac{32}{12} fr_C J_{om} = 2.67\, fr_C J_{om} \tag{2.17}$$

in which:

S_{ox}^{C} = oxygen demand for carbon oxidation per day in kg/m³/d

J_{om} = fraction of organic material decomposed in the period considered in kg/m³/d

The ammonia released during mineralization will be oxidised, according to:

$$2\,NH_4^+ + 4\,O_2 \rightarrow 2\,H_2O + 2\,NO_3^- + 4\,H^+$$

This results in an oxygen demand for nitrification given by:

$$S_{ox}^{N} = \frac{128}{28} fr_N J_{om} = 4.57 \frac{1}{C/N}\, fr_C J_{om} \tag{2.18}$$

in which:

S_{ox}^{N} = oxygen demand for nitrification in kg/m³/d

fr_N = nitrogen content of the organic material

C/N = carbon/nitrogen ratio of the organic material

The total oxygen demand S_{ox} under aerobic conditions is the sum of S_{ox}^{C} and S_{ox}^{N}.

In a natural system there is a continuous supply of fresh organic materials, such as litter from trees, dying roots and root exudates, vegetation residues and animal manures. Having a specific soil use, this will lead to a new equilibrium and a new organic matter content.

2.3 Presence of micro-organisms

2.3.1 Degrading Organisms

Many micro-organisms are able to degrade mineral oil. Schlegel (1992) explains this as follows. "Hydrocarbon-utilising bacteria are widely distributed; they can be isolated from arable, pasture and forest soils. Nor is the ability to utilise mineral oil as an energy source restricted to a few specialists among micro-organisms; it is found in numerous species of fungi and bacteria. These findings are also in accord with new analytical data about the composition of bacteria, plants and animals. Hydrocarbons are present in many organisms and are constantly synthesised by bacteria and plants; they belong for example to the wax-like substances that cover the leaves of plants. Hydrocarbons, therefore, should not be regarded solely as fossil relics of primary production by plants in prehistoric times, but also as secondary metabolites that are still being synthesised in considerable quantities by green plants". Also PAHs are not difficult to degrade as follows from the many publications on biodegradation of these substances (Overcash and Sims, 1983; Cerniglia and Heitkamp, 1989; Cerniglia, 1992; Agteren *et al.*, 1998). Aerobic conditions are necessary and in the absence of oxygen PAHs are persistent (Kai *et al.*, 2001).

Soil contains large numbers of bacteria, 10^6 to 10^8 or more per gram, using the plate count method (Boyd, 1988). Microscopic counts show higher number of bacteria (factor 10 to 100). Organisms in the largest group, not counted by plate, are the actinomycetes. Fungi are very common in soil and frequently the mass of fungi exceeds that of all other microbial groups in soil. A better appreciation of the fungal mass can be obtained by the lengths of their mycelium: as short as 10 meters per gram, but sometimes as long as 100 m per gram and occasionally in excess of 1000 meters per gram.

In dredged sediments the distribution of micro-organisms is homogeneous as shown by Boon *et al.*, (2000). They investigated a large landfill (100,000 m^3) filled with dredged sediment from the river Schelde and the Antwerp harbour basin, using denaturing gradient gel electrophoresis (DGGE). The obtained DNA fingerprints in all samples were comparable. Although this is only a proof for homogeneous distribution of the numerically dominant bacterial population and small differences were found for less abundant species, it is assumed that in a landfarm filled with sediment the starting position regarding the microbiological population is the same all over the landfarm. In principle the same developments of the microbiological population are possible at every place in the landfarm.

2.3.2 Acclimation time

The microbiological population is often not able to degrade a contaminant from the moment it is introduced in the soil. It is necessary that a degrading population will develop. This takes time and this is called the acclimation, adaptation or lag period. As soon as there are sufficient contaminant degrading organisms, this will be visible in a decrease of the measured concentration. For the degradation of easily degradable compounds, the presence of sufficient micro-organisms is not a problem (Alexander, 1994). Acclimation times from several days to months will occur. These are not fixed times and depend on concentration, environment, temperature, aeration status, and other, often undefined factors. Even under arctic conditions a degrading microbiological population will develop (Whyte *et al.*, 1999; Delille *et al.*, 2003). Under Dutch climate conditions adaptation also will not be a problem. Examples given in this thesis (Chapter 4 and 5) show that, if contaminants are available for degradation, the result is a rapid decrease in the measured concentration.

Sometimes, if a high concentration of a contaminant is present an apparent acclimation time will be measured. For the degradation a population of degrading organisms must grow. In the beginning the population will be small and the amount degraded will be too small to be measured. As soon as a large population exists, degradation will be visible. The presence of degrading micro-organisms is not considered as a problem in this thesis, because the treatment times of the described processes is much longer than the acclimation time. Landfarming as described in this thesis is a process of several years. The reported acclimation times can be ignored even when the acclimation time is several months.

2.3.3 Threshold value of contaminants

The concentration of the carbon source should be high enough to satisfy the needs for maintenance, energy and for processes that lead to increase in cell size, growth and multiplication. There must be growth to have detectable decrease of the contaminant concentration. If the initial concentration is to low, no grow of the original population will occur, resulting in a non-detectable decrease. The concentration at which no degradation will occur is the threshold concentration. Threshold values published are often based on laboratory studies in which the concentration of the contaminant has been varied, and threshold values of approximately1 µg/l have been found (Alexander, 1994).

At the start of landfarming, a threshold value is not a problem. Bioremediation is necessary because the concentration is high enough to cause effects. The population of degrading micro-organisms present will grow and degradation will occur. After a certain time period of treatment, the concentrations will decrease below the threshold values. However the situation of this moment cannot be compared with the situation at the threshold laboratory experiments. There is already an active population of micro-organisms. Degradation will continue even if the concentration of the contaminant becomes lower then the threshold value. At a low concentration, however, there will be a decrease in population. The probability of observing an active micro-organism will decrease, resulting in a slower degradation.

2.3.4 Distribution of organisms in sediment and soil

As discussed in Section 2.3.1, soil contains a large number of micro-organisms, but this should also be regarded on a smaller scale, the scale of the organism itself. Micro-organisms cannot be present at every place in the soil and are present in soil pores, which must be large enough to contain the organism. Soil pores are 40% (average) of the soil volume. Therefore, micro-organisms are not present in 60% of the soil volume. If this is the mineral part it is less interesting, because organic contaminants are mostly adsorbed on or absorbed in organic matter. Soil pore space can be distinguished in:

- Macro-pores.
- Pores between macro-aggregates.
- Pores between micro-aggregates.
- Pores within micro-aggregates.

The size of the pores is important for the microbial life. There must be enough places to live. Bacteria (2-4μm length and 0.2μm thick) can be present in very small pores. Nematodes can be found in pores between 30 and 90 μm (Hassink, 1995). Several nematodes are grazing on bacteria and as a consequence the number of bacteria in these pores is small. In pores not accessible for nematodes, the number of bacteria is larger. Hassink found a positive relation between the volume of pore space made up by pores between 0.2 and 1.2 μm and the number of bacteria. This explains the higher number of bacteria in clay soils compared to the number in sandy soils. The pores within the micro-aggregates are not accessible for micro-organisms (Elliott and Coleman, 1988). On these places the probability of meeting a micro-organism is zero. On all other places it is larger and can be one on places with a large number of bacteria. Only on the places with a micro-organism, degradation may occur and presence of oxygen and diffusion of the contaminant to these sites has to be stimulated.

The probability of finding a degrading micro-organism will be maximal in the pores having a diameter of about 1μm. For optimal transport of the contaminant to the micro-organism, this pore has to be water filled. On the contrary, larger pores have to be air filled to be able to supply the necessary oxygen. Assuming that optimal degradation occurs if the pores larger than 1.2 mm are air filled, it can be calculated that this will occur at a soil water potential[2] (see also 2.4) of < -2344 mbar. The soil water potential is a measure for the energy status of water in soil and has a small negative value in large pores and reaches high negative values in small capillary pores. The relation between water filled pore size and soil water potential is given in Table 2.6. Bacteria will be present in pores presented in the upper part of the table.

Table 2.6 Soil water potential at given maximum diameter of water filled pores.

Maximum diameter water filled pore d_{max} in μm	Soil water potential in mbar
0.2	-14125
1.0	-2818
1.2	-2344
2.0	-1380
10	-282
30	-91
90	-31

At soil water potentials of -2344 mbar and higher soils are completely aerobic. At a soil water potential of -14,125 mbar, which is close to the wilting point of -16,000 mbar (plant roots are no longer able to extract water from soil), also the bacteria filled pores are air filled and transport of the contaminant from the sorption site to the micro-organisms is no longer possible. These low soil water potentials can only be reached at the soil surface or in the root zone, because a high evaporation of water is needed.

Under Dutch conditions the water content below the root zone will be near field capacity. When the groundwater table is stable and at shallow depth, field capacity is in hydrostatic equilibrium with the groundwater table. With a deep groundwater table, field capacity general shows soil water potential of about -300 mbar (Koorevaar *et al.*, 1983). At this value all pores smaller than 10 μm are filled with water. Below the root zone the oxygen consumption can be the limiting factor as

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[2] Soil water potential is a measure for the energy status of water (Hillel, 1980). It is formally defined as the amount of work that must be done per unit of quantity of pure water in order to transport reversibly and isothermally an infinitesimal quantity of water from a pool of pure water at a specified elevation at atmospheric pressure to the soil water (at the point under consideration). In practise the potential is not measured by transporting water as per definition, but by measuring another property related to the potential (e.g. hydrostatic pressure, elevation, etc).

described in 2.4. Depending on the soil type there will be either enough air filled pores to supply the bacteria with oxygen, or not enough, resulting in partly anaerobic conditions.

2.3.5 Effect of temperature on activity

Biological activity increases at higher temperature. The activity of soil micro-organisms at different temperatures is presented in Figure 2.6. A temperature of 10 °C is taken as reference temperature. The temperature at different depths in the landfarm has been calculated according to Rijtema *et al.* (1999) as will exist in Petroleum Harbour sediment based on an average temperature year in The Netherlands (Figure 2.7).

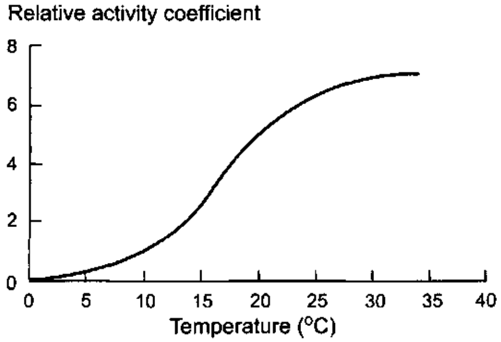


Figure 2.6 Relative activity coefficient of micro-organisms in soil (relative to value at 10 °C). Rijtema *et al.* (1999) based on data collected by Kolenbrander (personal communication, 1977).

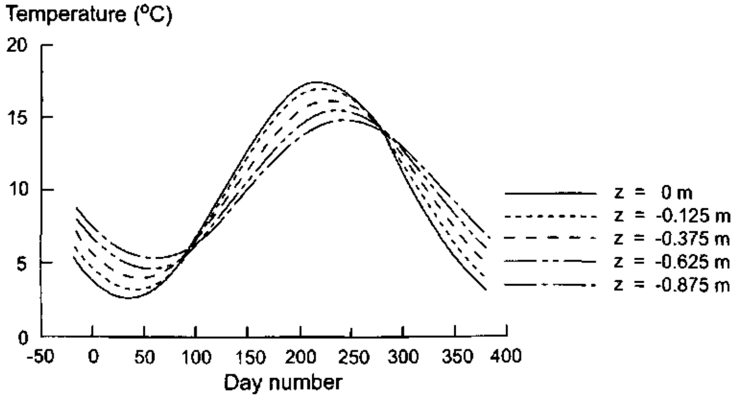


Figure 2.7 Temperature on different depth in the landfarm Petroleum Harbour (based on average year data, KNMI, 2004).

There is a strong effect of the temperature on the activity in the temperature range between 10 and 20 °C. During summer the highest temperatures are obtained at the surface layer, resulting in a much higher activity at that layer. In winter the opposite is the case and lowest temperatures are present at the surface. The effect of the temperature in winter on the activity is comparable in all layers; the activity is low. If it is possible to increase the average temperature in the landfarm to 20 °C, the relative activity will increase to 4.92. At this temperature the soil micro-organisms are more than 3 times as active as under natural temperature conditions. This is effective if the activity of micro-organisms is the limiting factor and no other limiting factors are present. Maliszewska-Kordybach (1993) showed that a temperature increase from 10 to 25 °C gave an increase of the degradation rate with a factor of 2-4 for spiked PAHs. These PAHs are available for degradation if no other limitations are present. If the availability of PAHs is limited (Section 2.2) or the supply of oxygen (Section 2.5) is limited the increase of temperature will be less effective

Combining the data in Figure 2.6 and 2.7 gives the relative activity at different depths as presented in Table 2.7. The average temperature is almost the same on all depth, but this must not lead to the use of the average activity. At the surface the difference between the minimum and maximum activity is much higher compared to lower depths. At the highest activities most of degradation will occur. In modelling (see section 2.5) of degradation it is therefore necessary to use a variable temperature.

Table 2.7 Relative calculated activity of micro-organisms in the Petroleum Harbour landfarm.

Depth (m)	Average temperature (°C)	Relative activity		
		Average	Min.	Max.
0	9.96	1.49	0.17	3.69
0.125	9.96	1.44	0.20	3.36
0.375	9.97	1.35	0.24	3.10
0.625	9.97	1.28	0.28	2.84
0.875	9.98	1.22	0.32	2.58

2.4 Presence of oxygen

Oxygen transport in dredged sediment is limited by the absence of air filled pores. Oxygen must diffuse through the water, which is a slow process and most part of sediments stays anaerobic. During dewatering and ripening (formation of physically stable soil aggregates) dredged sediment is changed into a structured soil. In the developed soil, part of the water (moisture) in the pores between soil particles is replaced by air and oxygen can reach larger depths. It is possible to predict the air filled part using basic soil properties (clay content, organic matter content) and the soil water potential. In landfarming the depth containing sufficient oxygen is an important parameter, because this sets the thickness of the layer to apply. Rijtema *et al* (1999) developed theories in order to describe the aeration in soils. In the following paragraphs the applicability of these theories for landfarming sediments will be discussed.

During dewatering and ripening of dredged sediment the following visible processes occur:

Compaction of the sediment layer.

- Development of cracks between large soil aggregates.
- Aeration of smaller aggregates (colour changes from black to brown).
- Finally a soil is obtained on which vegetation grows.

Gas in pores in dredged sediments, commonly indicated as soil air, shows the same composition as the overlying atmosphere in the upper few millimetres of the top layer. The aerated fraction in this part of the top layer, containing sufficient oxygen for biodegradation, is large. In sediments and soils many processes occur, of biological nature, which cause consumption of oxygen and a continuous change in the composition of the soil air. The aerated fraction decreases with depth. Exchange with the atmosphere occurs by diffusion, which is a slow process. The fact that gas diffusion in the liquid phase proceeds roughly 10^4 times slower as does diffusion in the soil air, explains the huge influence of soil moisture content on the gas phase composition and the exchange with the overlying atmosphere. The higher the moisture content, the slower the exchange.

In order to be able to give a mathematical description of the aerated fraction in dredged sediment it should be realised which factors have to be considered:

- Oxygen consumption. Organisms living in soil consume oxygen. The amount consumed depends on the amount and the degradability of the organic matter. This aspect is already discussed in Section 2.2.3.
- Transport of oxygen. Oxygen has to be transported (by diffusion) to the places where it is consumed. This is strongly related with the following factors:
    - Soil structure. Aeration will be better in a soil with a large air-filled pore volume with connected pores. In sediment the soil structure has to be developed and volumes are changing during this development. In several soil types cracks are developed during dewatering. These cracks are the main pathways that enable oxygen to diffuse to larger depths in heavy clay soils and dredged sediments.
    - Moisture content. Pores filled with water decrease the possibility of oxygen to diffuse in the soil. The moisture content depends on soil characteristics in combination with supply and removal of water.

In general the aerated soil fraction will be higher in a well-structured soil with low moisture content and low oxygen consumption (low organic matter content). Vermeulen *et al.* (2004) described methods to measure physical properties and results of measurements to be used as input parameters in models describing physical ripening of sediments. In this chapter the factors having influence on the structure of sediment in a landfarm are discussed more general and are limited to the processes during dewatering occurring in the first years of landfarming. To be able to give prediction of the aerated fraction of sediment theories of Rijtema *et al.* (1999) have been used. At first, the above mentioned factors are described, which will be combined to a relation which gives the aerated fraction as a function of general soil properties.

2.4.1 Basic parameters of sediments

General properties of soils are described with clay- and organic matter content and these properties are used to classify soils (Janssen *et al.*, 1990). Sediments however are more voluminous and cannot be described using soil classification. After dewatering and ripening this becomes possible, because then the sediment has been changed into a soil. The most important sediments investigated on the landfarm Kreekraksluizen and described in this thesis originate from the Petroleum Harbour in Amsterdam and the harbour of Wemeldinge (see also Chapter 4). In order to relate the physical processes described below to processes occurring in the landfarm on Kreekraksluizen, the basic parameters of the Petroleum Harbour and Wemeldinge sediment are presented in Table 2.8. Values were measured in sediment samples taken from or measured on the landfarm Kreekraksluizen described in Chapter 4. Values are used in further calculations.

Table 2.8 Physical properties of Petroleum Harbour and Wemeldinge sediment.

			Petroleum Harbour	Wemeldinge
Fraction clay	fr_{cl}	kg/kg	0.259	0.083
Fraction organic matter1)	$fr_{o.m}$	kg/kg	0.091	0.075
Density solid material	ρ_{spec}	kg/m^3	2567	2568
Volume solids initial	V_{solids}	m^3/m^3	0.276	0.333
Volume solids after dewatering and ripening (2003)2)	V_{solids}	m^3/m^3	0.369	0.437
Dry density initial	ρ_d	kg/m^3	708	855
Dry density after dewatering and ripening (2003)2)	ρ_d	kg/m^3	947	1122

1) Average value original sediment and dewatered sediment

2) Presented values, measured in 2003, were already obtained in 1999. The landfarm was started in 1994.

2.4.2 Volume changes of sediment during dewatering and ripening

Physical ripening is the process that changes low dry bulk density and water saturated dredged sediment into a well usable soil (Vermeulen *et al.*, 2003). The physical ripening results in increasing dry bulk density of the sediment and decreasing water content, causing shrinkage of the sediment and reduction of the height of the sediment. Cracks that develop due to this shrinkage improve the aeration and hydraulic permeability of the landfarm. Development of aerobic micro-organisms is not possible without physical ripening.

In water and material balance studies the solid phase is generally considered as being an inert, non-compressible material. It means that the volume density and the spatial distribution of the solid phase do not alter with time. In newly constructed landfarms three processes play an important role. They are: 1) Compaction, 2) Biodegradation of organic materials (both natural organic matter and contaminants), and (3) The combined effects of swelling and shrinking. The first two processes are irreversible i.e. compaction of the solid phase under influence of the top load and biodegradation as a consequence of biological activity. The soil compaction reduces the pore volume, whereas biodegradation of the natural organic matter results in an increase of the pore volume. The final result of these two time dependent processes is the subsidence (drop of the surface level) of the landfarm. The swelling and shrinkage process is a reversible one that can be considered as an instantaneous one.

As a consequence of these processes a considerable change in the volume, as a function of time and water content will be present. So the solid phase cannot be considered as inert and non-compressible material, and in studies in which the distribution of moisture and air over the pore volume are involved, these effects must be considered.

Compaction

Dredged sediments are voluminous and after dredging and transport to a landfarm their volume will reduce due to the load of upper laying sediment on underlaying sediment. On the landfarm this load is higher than in the original water body, because the upwards pressure in water is missing. Compaction is an irreversible process. For the calculation of compaction the model given by Rijtema *et al.* (1986) is followed, in which the subsidence (drop of the surface level with respect to the fixed bottom layer) of the applied layer of sediment as a result of its own load is described:

$$Z = \frac{1}{C_c}\left[\left(\frac{1}{2}\Delta H + L_a\right)\ln\left(\frac{\frac{1}{2}\rho_w \Delta H + \rho_w L_a}{\frac{1}{2}\rho_w \Delta H}\right) - L_a\right] \tag{2.19}$$

where:

Z = final subsidence of the landfarm due to irreversible compaction in m
C_c = compressibility constant of the dredged sediment in m/m
L_a = initial layer thickness of the dredged sediment on the landfarm in m
ρ_w = initial wet volume weight of the dredged sediment in kg/m^3
ΔH = layer thickness without top load in m

From this equations follows that the subsidence of an unloaded sediment layer will approach to zero, when the considered layer thickness ΔH becomes very small. The compressibility constant C_c depends on the pore volume in the dredged sediment. The packing density of the material approaches its maximum value when a very large top load is present.

Calculations have been performed for the Petroleum Harbour and Wemeldinge landfarms with an initial sediment height of 1 m and using experimental data given in Table 2.8. The calculated subsidence for Petroleum Harbour and Wemeldinge were respectively 5.9 and 9 cm. Subsidence is the result of compaction by the weight of the sediments upon itself. Because of the limited height in a landfarm, the value is relatively low. Including the ripening process as described below, higher subsidence as observed in landfarms can be expected. Generally this irreversible subsidence can be considered as an instantaneous process in landfarm operations compared to the required treatment time of the landfarm.

Physical ripening of sediments

Shrinkage process

After compaction and removal of the excess of water, the sediment has to be dewatered further in order to introduce oxygen. Water filled pores have to be replaced by air filled pores. Gas filled pores are not only created in aggregates, but also between aggregates. The latter are the result of a shrinking process; the volume of sediment is larger than the volume of dewatered ripened soil. During dewatering, three successive shrinkage phases can be distinguished (Haines, 1923; Bronswijk, 1991; Kim, 1992)

1. Normal shrinkage: Volume decrease of clay aggregates is equal to moisture loss. The aggregates remain fully saturated.
2. Residual shrinkage. Upon drying the volume of the aggregates still decreases, but moisture loss is greater than volume decrease. Air enters the pores of the aggregates.
3. Zero shrinkage. The soil particles have reached their most dense configuration. Upon further moisture extraction, the volume of aggregates stays constant. Moisture loss is equal to increase of air volume in the aggregates.

Shrinkage leads to formation of cracks between developed soil aggregates. In the beginning, both cracks and aggregates are large (respectively around 1 and 20 cm) but the dryer the sediment the smaller the cracks and aggregates will be. The fraction of linear extensibility (fr_{linex}) is a measure of the difference of the aggregate volume of the original water saturated sediment and the aggregate volume of the developed soil at dry conditions (after dewatering and ripening) and is defined as:

$$fr_{linex} = \sqrt[3]{\frac{V_{sat}}{V_{dry}}} - 1 \qquad (2.20)$$

in which:

fr_{linex} = fraction of linear extensibility

V_{sat} = volume original water saturated sediment in m^3

V_{dry} = volume of the developed soil aggregates in a dry state in m^3

In a thick layer of sediment applied on the landfarm and under Dutch climate conditions, the driest conditions will be obtained if roots of plants are not able to subtract more water (wilting point). Only at the surface dryer conditions can be obtained. In most soils the maximum shrinkage is obtained at the wilting point. Data given by Bronswijk and Evers-Vermeer (1990) were used by Rijtema *et al* (1999) to determine a relation between the fraction of linear extensibility at wilting point ($fr_{linex,wp}$) and the clay and organic matter content of the soil. In this relation $fr_{act} = fr_{cl} + 2.5 \cdot fr_{om}$ was taken as the soil variable.

$$fr_{linex,wp} = 0.2 fr_{act} + 0.08 - \sqrt{(0.2 fr_{act} + 0.8)^2 - 0.072 fr_{act} + 0.0051)} \qquad (2.21)$$

Using this equation and the data in Table 2.8 the fraction of linear extensibility at wilting point ($fr_{linex.wp}$) for the ripened Petroleum Harbour and Wemeldinge sediment can be calculated as respectively 0.139 and 0.072 m/m. These values were used as maximum values in further calculations.

In the field, volume changes of the soil aggregates become visible as cracking and subsidence. In ripened soils shrinkage is a reversible process and extends uniformly in all directions (Bronswijk, 1991). It means that a unit volume of soil decreases equally in size in both horizontal directions and in the vertical direction (isotropic shrinkage). Shrinking will continue and at certain soil water potential the maximum packing density of the soil aggregates is obtained. A further decrease of the moisture volume until wilting point then takes place with a constant aggregate volume and air entering into the aggregates.

For most ripened clay soils shrinkage is isotropic (shrinkage is the same in all dimensions). Shrinkage characteristics of field sediments can deflect markedly (Bronswijk, 1986). In the field, volume changes of the soil aggregates become visible as cracking and subsidence and the crack volume becomes smaller. In a study on unripe soils, Rijniersce (1983) introduced a geometry factor *rs* (Equation 2.22), which determines the partition of total volume change over layer thickness and crack volume.

$$V_{aggregates} = (1 - fr_{linex})^{rs} \tag{2.22}$$

where:

rs = dimensionless geometry factor.

In case of only subsidence without cracking *rs* equals 1. In case of cracking without subsidence *rs* becomes infinite. For all other *rs*-values, both cracking and subsidence occur simultaneously with the following division: $rs = 3$: isotropic shrinkage; $1 < rs < 3$: subsidence dominates cracking and $rs > 3$: cracking dominates subsidence. For the majority of soils, $rs = 3$, i.e. shrinkage and swelling are isotropic from saturation to oven dryness. Using this terminology for ripened sediment results in general relations between material volume change and subsidence of a sediment volume at specific moisture content. With these relations it is possible to calculate the layer thickness of the sediment and the area and volume of the cracks developed during shrinking. The cracks are important for aeration of the sediments.

Layer thickness at moisture content θ z_θ:

$$z_\theta = (1 - fr_{linez}).z_{sat} \tag{2.23}$$

Crack area (A_{cr}) and crack volume (V_{cr}) at the same moisture content:

$$A_{cr} = 1 - (1 - fr_{linex})^{rs-1} \tag{2.24}$$

$$V_{cr} = (1 - fr_{linex})[1 - (1 - fr_{linex})^{rs-1}] \tag{2.25}$$

In the approach followed here, *rs* is either a constant or varying with water content. Use of a variable geometric factor *rs* was necessary in the calculations for Petroleum Harbour and Wemeldinge sediment presented further in this chapter to assure that al volumes calculated were consistent. The geometric factor is not constant and depends on the soil moisture content. It starts with 3 at moisture contents near saturation and may decrease to about 2.6 at lower moisture contents. For Petroleum Harbour and Wemeldinge sediments, calculated values are presented in Table 2.13.

Characterization of ripening

The physical ripening can be characterized by a ripening coefficient as is given by Pons and Zonneveld (1965), using the empirical expression:

$$n = (\theta_w - 0.2.fr_{sa})/(fr_{cl} + b.fr_{om}) \tag{2.26}$$

where:

n = soil ripening factor

θ_w = water content of the saturated sediment in kg/kg

fr_{sa} = fraction of sand (= $1.0 - fr_{cl} - fr_{om}$) in kg/kg

fr_{cl} = fraction of clay in kg/kg

fr_{om} = fraction of organic material in kg/kg

b = ratio of water adsorbing capacity between organic material and clay minerals. The factor b generally is given the value 3.

Pons and Zonneveld (1965) give a classification of soil ripening as presented in Table 2.9.

Table 2.9 Classification of the soil ripening factor n, according to Pons and Zonneveld (1965).

Soil ripening factor *n*	Classification
< 0.7	ripened soil
0.7 – 1.0	almost ripened soil
1.0 – 1.4	half ripened soil
1.4 – 2.0	mostly unripe soil
>2.0	unripe soil

In dredged sediment four zones can be recognised (Vermeulen *et al.*, 2003):

- Unripe consolidated sediment below the water table.
- Half-ripe soil with a coarse to very coarse prismatic structure.
- Nearly ripe soil with coarse aggregates.
- Ripe soil with medium to fine aggregates at the top.

The expression of Pons and Zonneveld can be rewritten as follows in order to calculate the saturated moisture fraction at different degrees of ripening. Results of this calculation for Petroleum Harbour and Wemeldinge sediments on the landfarm are given in Table 2.10:

$$\theta_{sat} = \frac{n\,(fr_{cl} + b.fr_{om}) + 0.2.fr_{sa}}{1000\,/\,\rho_{spec} + n\,(fr_{cl} + b.fr_{om}) + 0.2.fr_{sa}} \qquad (2.27)$$

where:

θ_{sat} = moisture fraction of the saturated sediment in m^3/m^3

ρ_d = specific weight of the sediment in kg/m^3

Table 2.10 Calculated values at different degree of physical ripening using Equation 2.27 for moisture fraction (m3/m3) and specific weight (kg/m3) for Petroleum Harbour and Wemeldinge sediment.

Ripening factor	Petroleum Harbour		Wemeldinge	
n	θ_{sat} m^3/m^3	ρ_d kg/m^3	θ_{sat} m^3/m^3	ρ_d kg/m^3
0.7	0.563	1121	0.497	1292
1.0	0.630	951	0.550	1155
1.4	0.692	791	0.606	1011
2.0	0.754	632	0.668	852

From the year 2001 the landfarms of Kreekraksluizen were fully ripened and ripening factors < 0.7 were measured. Only at higher depths incidentally higher values between 0.7 and 1.0 were measured. This is also caused by sampling; small ripened aggregates could not be used for measurements and suitable larger aggregates are often less ripened (worst case situation).

Comparison of different volume changes

Calculated data on the pore volume in sediment after compaction, compaction and shrinking and using the formulation of Pons for a ripened soil are presented in Table 2.11. For shrinking both the reduction in layer thickness and volume reduction are taken into account. The calculated values are compared with measured values (Table 2.8) and representative for dry and ripened sediment).

Table 2.11 Calculated and measured pore volume (fraction of total volume) of sediments after compaction, dewatering and ripening.

	Petroleum Harbour	Wemeldinge
Initial (measured)	0.724	0.667
After physical ripening (predicted according Pons)	0.563	0.497
After compaction (predicted)	0.707	0.634
After compaction and physical ripening (measured)	0.631	0.563

The calculated values for the situation after ripening (predicted according Pons) should be obtained if the sediments develop in soils with normal (sub)soil properties. This means that in dewatered ripened sediment, the pore volume is higher then expected from classification of the sediment as a soil. Soil particles in landfarmed sediment are packed less dense and the shrinking volume is partly included in the structure. For landfarming this is a positive result, because a higher pore volume enables a better supply of oxygen. This is taken into account in formulation of the shrinkage on such a way that the calculated pore volume after shrinkage is the same as the measured one.

Soil moisture in developed soil

After dewatering and ripening of sediments, both the distribution of pore sizes and the soil moisture characteristics depend on the granular composition and the density. In soils, the moisture content depends on the soil water potential. This soil water potential is a measure of the energy status of water. Under saturated conditions, all pores are filled with water; and therefore the soil water potential is positive (hydrostatic pressure). Under unsaturated condition, but in equilibrium with the groundwater table, it is the distance to the groundwater table (negative value). Under dry conditions in summer the soil water potential can reach very low values and stops at a value of -16000 mbar, and roots are not able to extract water anymore. At soil water potential of 0 mbar the moisture content is equal to the pore volume. With decreasing soil water potential this content becomes lower and moisture will be replaced by air. The large pores will be the first in which water is replaced by air. Small pores in aggregates will be kept filled with water. During wetting hysteresis occurs and not the same curve as found for drying will be followed. The soil water potential at which water is replaced by air depends on the pore diameter (Koorevaar *et al.*, 1983):

$$\psi = \frac{-400\sigma}{\rho_l g d_{\max}} \tag{2.28}$$

where:

ψ = soil water potential (mbar)
σ = surface tension of water = 0.07 N/m
ρ_l = density of the liquid phase = 1000 kg/m^3
g = magnitude of gravitational field strength = 9.81 N/kg
d_{max} = maximum diameter of a water filled pore (m)

Rijtema (1969) presented on the basis of the available data from literature a first series of physical parameters for standard soils. Wösten *et al.* (1994) presented a series of measured data of soil moisture characteristics for Dutch soils using the method given by van Genuchten (1980). All these data were averaged by Rijtema *et al.* (1999) for a number of soil groups, resulting in a series of standard soils. They considered subsoils, which are stable non-compressible materials. A selection of these values for typical soil types is presented in Table 2.12. This table shows the large differences in pore volumes and the part filled with water that can be expected with landfarming sediments of different origin. If after dewatering and ripening loamy sand is obtained, half of the pore volume is already gas-filled at a soil water potential of -100 mbar (groundwater level at 100 cm below surface). Under the same conditions, only 10% of the pore volume in silty clay is gas-filled.

Table 2.12 Soil moisture content as volume percentage in relation to soil water potential for standard subsoils, after Rijtema et al. (1999).

Soil type	Soil water potential in mbar								
	0	-10	-31	-100	-250	-500	-2500	-16000	-10^6
Loamy sand$^{1)}$	34.5	32.3	28.0	17.3	10.4	7.3	3.5	1.7	0.8
Silty clay	56.1	55.8	54.4	51.2	46.8	42.9	33.8	25.3	8.5
Clay loam	49.0	48.4	46.7	41.7	35.3	30.4	19.4	11.6	6.2
Silty clay loam	46.3	45.8	44.1	37.2	30.5	24.1	14.0	8.5	6.0
Peat	87.3	86.1	82.6	72.3	60.0	48.9	29.6	19.1	7.8

1) average value of loamy fine sand loamy medium fine sand and loamy medium coarse sand

Sediments, having comparable composition, have much higher moisture contents than soil. It can be assumed that the pore volume after dewatering and ripening can be predicted using the basic properties, but this is only true if the compaction in the sediment is high enough that the density of a subsoil is obtained. Comparing the pore volumes of the Petroleum Harbour and Wemeldinge sediment during landfarming (Table 2.11), the soils developed on the landfarm have a higher pore volume (lower bulk density) than a subsoil with the same properties. Therefore it is not possible to replace the soil moisture characteristics of the ripened landfarmed sediment by characteristics of standard soils directly. In practice of landfarming the characteristics of the ripened sediment will always be an unknown factor. To obtain the soil moisture characteristics the following approach is used;

Taking into account the measured bulk density of the sediment, it is assumed that the dredged sediments are heterogenic mixtures of mineral soils and organic materials. In order to be able to describe the soil moisture characteristic of the ripened sediments the characteristics of peat are used to represent organic matter and clay loam to represent the mineral part of Petroleum Harbour sediment. Instead of clay loam, loamy sand is used to represent the mineral part of the Wemeldinge sediment considering the dredged sediments as competing imperfect mixtures of organic soil and mineral soil. Concurrence between these basic materials is introduced by multiplying the calculated result with θsat (measured)/θsat (calculated). All these calculations yield the soil moisture characteristics as presented in Table 2.12.

Physical parameters of Petroleum Harbour and Wemeldinge sediment

Making use of the measured value after ripening and the theories in previous sections the data on physical properties as given in Table 2.13 have been calculated. Values are presented for different soil water potentials.

The theories above can be applied if a structured soil is obtained during landfarming of sediment. When a developed soil is sensitive to slaking (deterioration of soil structure by rainfall), the pore volume will reduce in wet periods because in those soils dispersed silt and clay particles will fill the volume between coarse particles. Cultivation and soil improvement (i.e. adding of compost) will be necessary to increase the pore volume of the treated sediment again. The chance of slaking increases with less cohesion as present in soils with low organic matter content. Increasing clay content also increases the chance of slaking, although the stability increases again at high clay content. Soils with approximately10% clay or more then 50% silt are most sensitive for slaking (Schneider and Huinink, 1990). In the experiments described in this thesis structured soils were obtained. The Wemeldinge sediment was most sensitive for slaking as observed in the container experiments described in Chapter 6.

Table 2.13 Calculated physical parameters at different soil water potentials for Petroleum Harbour and Wemeldinge sediment during dewatering.

Variable	Soil water potential in mbar								
	0	-10	-31	-100	-250	-500	-2,500	-16,000	-10^6
	Petroleum Harbour								
Soil moisture content m^3/m^3	0.631	0.623	0.599	0.529	0.443	0.370	0.230	0.143	0.067
fr_{linex}	0.000	0.001	0.008	0.035	0.068	0.102	0.139	0.139	0.139
Geometry factor r_s	3.000	2.983	2,969	2.894	2,792	2,697	2,609	2,609	2,609
Layer thickness m/m	1.000	0.999	0.992	0.965	0.932	0.898	0.861	0.861	0.861
Crack area m^2/m^2	0.000	0.002	0.016	0.065	0.119	0.167	0.214	0.214	0.214
Crack volume m^3/m^3	0.000	0.002	0.016	0.064	0.111	0.150	0.184	0.184	0.184
	Aggregate properties								
Aggregate volume m^3	1.000	0.992	0.968	0.898	0.882	0.739	0.677	0.677	0.677
Solid volume m^3/m^3	0.369	0.372	0.381	0.411	0.418	0.499	0,545	0.545	0.545
Moisture content of aggregates m^3/m^3	0.631	0.628	0.619	0.589	0.502	0.501	0.340	0.211	0.099
Air-filled pore volume of aggregates m^3/m^3	0.000	0.000	0.000	0.000	0.000	0.000	0.115	0.244	0.356
	Wemeldinge Harbour								
Soil moisture content m^3/m^3	0.563	0.546	0.509	0.404	0.314	0.249	0.146	0.091	0.037
fr_{linex}	0.000	0.006	0.019	0.061	0.074	0.074	0.074	0.074	0.074
Geometry factor r_s	3.000	2.980	2.945	2.826	2.786	2.786	2.786	2.786	2.786
Layer thickness m/m	1.000	0.994	0.981	0.939	0.926	0.926	0.926	0.926	0.926
Crack area m^2/m^2	0.000	0.012	0.037	0.109	0.128	0.128	0.128	0.128	0.128
Crack volume m^3/m^3	0.000	0.012	0.036	0.102	0.119	0.119	0.119	0.119	0.119
	Aggregate properties								
Aggregate volume m^3	1.000	0.983	0.946	0.841	0.808	0.807	0.807	0.807	0.807
Solid volume m^3/m^3	0.437	0.445	0.462	0.520	0.541	0.541	0.541	0.541	0.541
Moisture content of aggregates m^3/m^3	0.563	0.555	0.538	0.480	0.389	0.311	0.180	0.113	0.046
Air-filled pore volume of aggregates m^3/m^3	0.000	0.000	0.000	0.000	0.070	0.148	0.279	0.346	0.413

2.4.3 Air filled pore volume in the sediment profile

After compaction and dewatering, an optimum landfarm must have enough air filled pores to ensure the supply of oxygen and enough water filled pores to stimulate biodegradation and to allow the possibility for diffusion of the contaminant. The accuracy of the forecast distribution between water filled and gas filled pores soil moisture extraction depends upon the accuracy to which the properties of the developed soil are known. The distribution between pore volumes is not only directly related to the soil physical properties, but is also dependent on the climate conditions, on the depth of the phreatic water level and on the plant root distribution in the unsaturated zone. This is illustrated in Figures 2.8 and 2.9 further in this section. The model BALANCE (Rijtema *et al*, 1999) is used in a multi-layered system for the calculation of the water balances per layer, starting from the following definitions:

- In its simplest form the moisture fraction in the root zone is assumed to be uniform with depth and in the absence of a water table in the root zone the moisture fraction at the end of the time step can be expressed as:

$$\theta_r = \frac{V_r}{Z_r} \tag{2.29}$$

where:

θ_r = moisture fraction in the root zone in m^3/m^3
V_r = moisture volume in the root zone in m^3/m^2
Z_r = thickness of the root zone in m

- The soil water potential at the top of the subsoil below the root zone equals the soil water potential of the root zone. The moisture fractions in the root zone and at the top of the unsaturated subsoil are described by interpolation of the soil moisture characteristics of both layers. The soil moisture in the subsoil is redistributed over the layers after rewetting of the root zone by precipitation. In this method of operation the effects of hysteresis and preferential flow are also more or less taken into consideration, as rewetting of the subsoil already starts in the model before the root zone is at field capacity.
- The minimum moisture volume present in the subsoil after maximum extraction through evapotranspiration is assumed to be bounded by the line describing the steady state situation for an upward capillary flux of 0.01 cm/d and the soil water potential at the boundary of root zone and subsoil at wilting point. By using this boundary condition the depth for 100% water saturation depends on the soil type.

With the data presented in Table 2.12 the moisture distribution for the minimum obtainable water fraction of subsoils can be calculated. Examples of this distribution for different soil types are presented in Figure 2.8 (Rijtema *et al.*, 1999). Two situations can be distinguished. The line representing equilibrium moisture distribution (field capacity) is representative for the winter period. The moisture distribution with a flux of 0.01 cm/d will be obtained in summer, when evaporation will exceed precipitation and capillary rise.

For all soils, the gas filled volume fraction in the root zone is high enough to supply sufficient oxygen. At the groundwater table the oxygen supply will be problematic, because no air filled pores are present. In between the root zone and the groundwater table, the characteristics of the presented soils are different. Important is the value for the brake point in subsoil moisture distribution (Z_{cr}) as indicated in Figure 2.8. Above this value the gas filled volume is still high. Below this value the gas filled volume becomes low for silty clay and peat and will also be low for heavier soils. For more sandy soils the gas filled pore volume at Z_{cr} is higher and consequently the decrease of this volume at higher depths is slower.

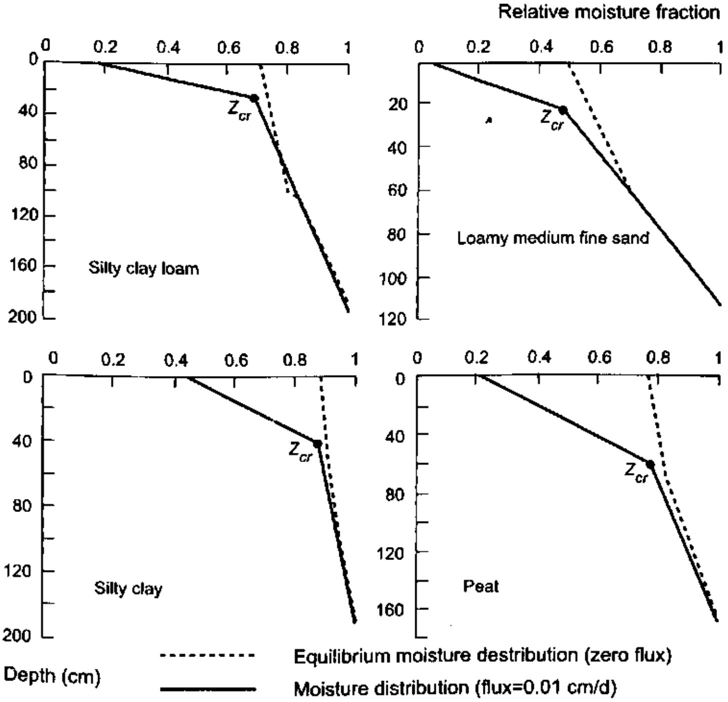
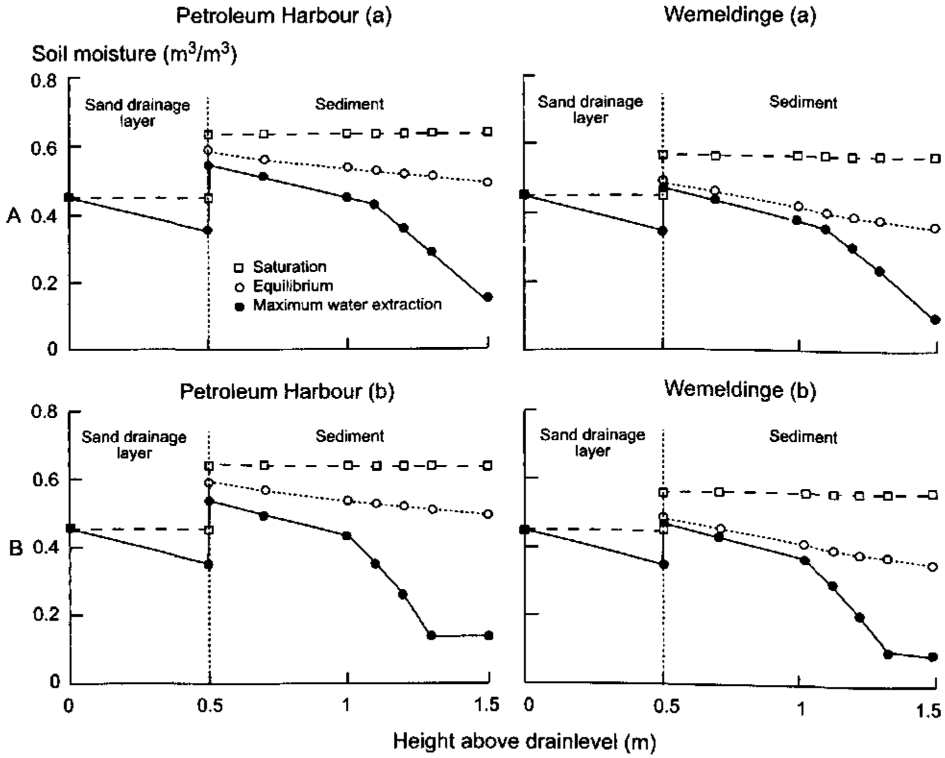


Figure 2.8 Soil moisture distributions in the unsaturated subsoil as a function of the depth below the effective root zone for different soil with the upper boundary at wilting point and a steady state capillary rise of 0.01cm/d (derived from Rijtema *et al.*, 1999). Z_{cr} = depth of brake point in subsoil moisture distribution.

The theory described above has been applied to the sediments of Petroleum Harbour and Wemeldinge. The calculated soil moisture distribution in Petroleum Harbour and Wemeldinge sediment as a function of the depth below the effective root zone is presented in Figure 2.9. In this figure, 1 meter of sediment is present on a drainage layer of 50 cm sand; the drainage level is set at -1.5 m below the surface. Three situations are distinguished. The upper line is the situation at complete saturation. The following line is the equilibrium situation, where the soil in the complete profile is at field capacity. This will be the situation when the evaporation is low (winter) and after sufficient time to achieve equilibrium after rain. The moisture fraction is relatively high and can be a limiting factor for oxygen diffusion to lower levels. The lowest curve gives the most optimal situation for oxygen supply, which can be obtained during summer. Due to the maximum extraction of water (evaporation), the upper boundary is at the wilting point and a steady state capillary rise of 0.01cm.d^{-1} is assumed. In this situation pores in the root zone are mainly air filled and the amount of air filled pores is high until Z_{cr} is attained. Below this depth the moisture fraction increases, until saturation at the drainage level or water table. It can be concluded from this figure that in summer a layer of 40 cm below the root zone will have a high air filled pore volume.

Figure 2.9 already shows the differences between the summer period with high evaporation (maximum extraction) and the situation in winter (equilibrium or saturated). The variation during the year is calculated in more detail for different depths in Petroleum Harbour sediment (Figure 2.10). The variation of the moisture content causes also a variation of the crack area (Equation 2.24). Results of these calculations are also given in Figure 2.10.


Petroleum Harbour (a)

Wemeldinge (a)

Petroleum Harbour (b)

Wemeldinge (b)

Figure 2.9 Soil moisture distributions as a function of the depth below the soil surface in Petroleum Harbour and Wemeldinge sediment. Above the drains (at -1.5 m below surface) a sand drainage layer of 0.5 m is present. (a) bare sediment; (b) sediment covered with vegetation with an effective root zone of 0.2 m. The maximum supply rate from the deeper layers by capillary rise equals 0.01 m/d, when the maximum water extraction rate has been reached.

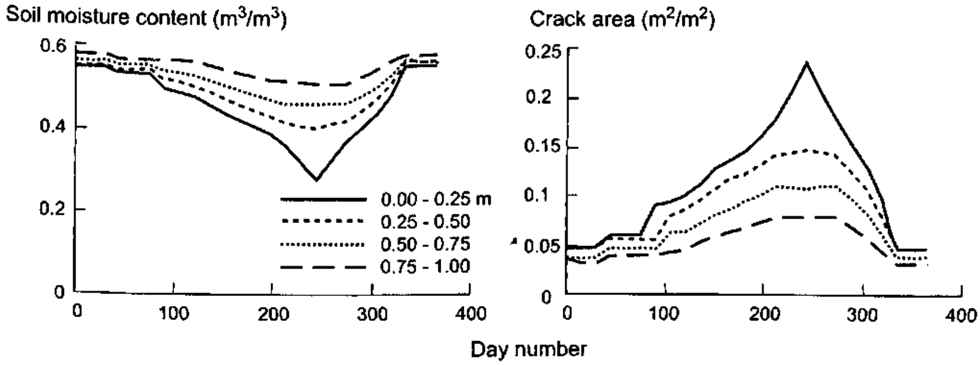


Figure 2.10 Variation of soil moisture content in aggregates and crack area on different depths during the year as calculated for Petroleum Harbour sediment.

2.4.4 Oxygen in aggregates

Vertical diffusion of oxygen in the gas phase in cracked soils is primarily governed by the number of the air filled cracks. The oxygen consumption in the soil takes place in the water saturated and partly aerated soil aggregates. Oxygen has to diffuse into the aggregates, where it may give full aeration in small aggregates, but in large aggregates the inside will stay anaerobic because oxygen is used for degradation of organic matter in the outer part of the aggregate.

The vertical inflow of oxygen by diffusion can be described using the total crack area, without considering the distribution of the crack width. Bronswijk (1991) gives the oxygen diffusion coefficient in cracked soils as:

$$D_{cr}^{ox} = \eta \cdot A_{cr} \cdot D_{atm}^{ox} \qquad (2.30)$$

where:

η = tortuosity factor with a value varying between 0.3 and 1.0.

D_{cr}^{ox} = oxygen diffusion coefficient in cracks

D_{atm}^{ox} = oxygen diffusion coefficient in air

Rijtema *et al.* (1999) give a method to calculate the aerated fraction f_{ae} of cylindrical aggregates, using the equation:

$$f_{ae} = 1-(1-(\frac{4c_{we}^{ox}D_{s}^{ox}}{S_{ox}r_{eq}^{2}})^{0.4})^{1.18} \qquad (2.31)$$

where:

c_{we}^{ox} = equilibrium oxygen concentration in water at the air/water boundary in kg/m^3

D_s^{ox} = diffusion coefficient of oxygen in pore water in m^2/d

S_{ox} = oxygen demand of sediment in kg/m^3/d

r_{eq} = equivalent radius assuming cylindrical aggregates in m

In Equation 2.31 the equivalent radius is the only unknown parameter. Knowing the equivalent radius of the aggregates it is possible to calculate the aerated fraction of the aggregates. The aeration of the aggregates by horizontal diffusion in the water saturated aggregates is strongly dependent on distribution of the size of the aggregates. Not only the crack area increases but also the number of aggregates, when the shrinking due to the evaporation surplus proceeds. In order to calculate the aerated fraction in aggregates it is necessary to have a relation between the equivalent radius of aggregates and the crack area. The approach to obtain this relation is described below.

It appeared that the maximum crack width in the Petroleum Harbour sediment was about 0.01 m at distances of about 0.20 m and in the Wemeldinge sediment slightly less. The hexagonal shape of the aggregates as introduced by Bronswijk (1991) is used to formulate an idealized approach for the calculation of the aggregate size as a function of the crack area. The surface area of cracked sediment is shown schematically in Figure 2.11.

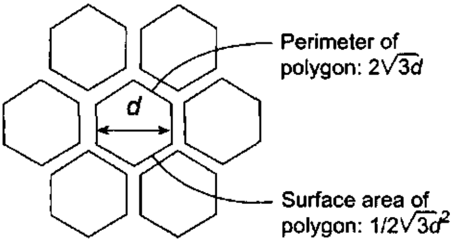


Figure 2.11 Geometry model of the crack pattern in harbour sediments. d = diameter of polygon.

The starting point for the calculations is completely saturated sediment with a surface area of 1 m^2. Introducing increasing numbers of aggregates per m^2 gives the area per saturated aggregate. The contribution of the aggregates to the crack area depends on the value d of the hexagonal aggregate. The maximum contribution to the crack width (W_{cr}) is 0.02d in Petroleum Harbour sediment, and 0.014d in the Wemeldinge sediment. An example of the calculation procedure for Petroleum Harbour sediment is shown in Table 2.14. The following calculation steps were necessary to calculate the crack area (A_{cr}), the shrinkage corrected value of d and the radius of the equivalent cylinder (r_{eq}) for different number of aggregates per m^2 (N):

I. Maximum surface area of the aggregate A_{max} (n) at given number of aggregates.
II. Maximum diagonal d_{max}(n)of the hexagonal aggregate.
III. Width of the cracks W_{crk}(n). The value for n=1 is based on field observations.
IV. Length of cracks L_{cr}(n).
V. Increase of the length of cracks ΔL_{cr} (n). (n-(n-1)).
VI. Increase of crack area ΔA_{cr}(n).
VII. Crack area A_{cr}(n).
VIII. Correction of d_{ag}(n) for shrinkage to give d_{corr}(n).
IX. Radius of the equivalent cylinder r_{eq} (n).

Table 2.14 Example of the calculation scheme of the relation between crack area (A_{cr}), The shrinkage corrected value of d_{cor} and the radius of the equivalent cylinder (r_{eq}).

	Number of aggregates per m^2(N)	4.619	10	20	25	30	35	40
	Calculation number (n)	1	2	3	4	5	6	7
Calculation step								
I	A_{max} (n) = (1/N (n)) (m^2)	0.2165	0,1000	0.0500	0.0400	0.0333	0.0286	0,0250
II	D_{max} (n) = $\sqrt{((2/\sqrt{3}).A_{max}(n))}$ (m)	0.5000	0.3398	0.2403	0.2149	0.1962	0.1816	0.1699
III	W_{crk}(n) = 0.01(d_{max}(n-1) + d_{maxg} (n)) (m)	0.0100	0.0084	0.0058	0.0046	0.0041	0.0039	0.0035
IV	L_{cr}(n) = $2\sqrt{3}.N.d_{max}$(n) m	8.00	11.77	16.65	18.61	20.39	22.02	23.54
V	ΔL_{cr} (n)= L_{cr} (n) – L_{cr} (n-1) m	8.00	3.77	4.88	1.96	1.78	1.63	1.52
VI	ΔA_{cr}(n) = 0.5W_{cr}(n). ΔL_{cr}(n) m^2	0.0400	0.0158	0.0141	0.0045	0.0037	0.0031	0.0027
VII	A_{cr}(n) = A_{cr}(n-1)+ΔA_{cr}(n) m^2/m^2	0.0400	0.0558	0.0700	0.0745	0.0781	0.0812	0.0839
VIII	d_{corr}(n) = $\sqrt{(1 - A_{cr}(n))}.d_{max}$(n) m	0.4899	0.3302	0.2317	0.2068	0.1884	0.1741	0.1626
IX	r_{eq} (n) =$[\sqrt{3}/(2\pi)]^{0.5}.d_{corr}$(n) m	0.2572	0.1734	0.1217	0.1086	0.0989	0.0914	0.0838

In the last calculation step, the hexagonal aggregates are transformed into cylindrical aggregates, giving the calculated equivalent radius r_{eq}. The result of this step wise calculation (equivalent radius r_{eq} of the aggregates as function of crack area A_{cr}) is presented in Figure 2.12. The relations can be expressed by the following equations:

Petroleum Harbour: $$r_{eq} = 0.706\exp(-25.3A_{cr}) \qquad (2.31)$$

Wemeldinge $$r_{eq} = 0.759\exp(-35.8A_{cr}) \qquad (2.32)$$

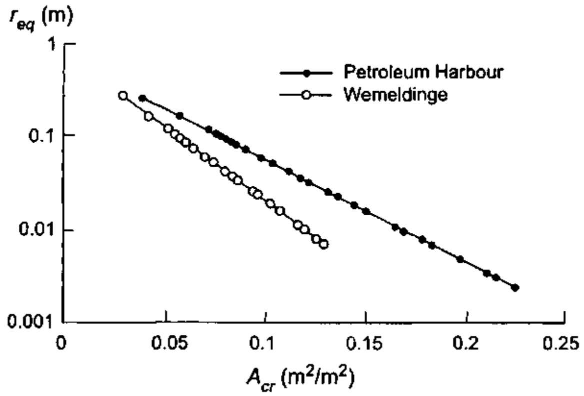


Figure 2.12: The relation between A_{cr} and r_{eq} in Petroleum Harbour and Wemeldinge sediments.

2.5 Modelling of processes in a landfarm

As shown in previous parts of this chapter the rate of aerobic degradation of contaminants does not depend on the presence of active degrading organism. They are present and a suitable population is quickly developed in aerated sediment. However micro-organisms are not present on every place in the soil. It will be necessary for contaminants to desorb and to diffuse to the degrading organism, which is a slow process. Creating wet conditions and an extreme reduction in the size of aggregates may stimulate the desorption rate, but this is not realistic under landfarm conditions. Wet conditions will give an aeration problem and it is not possible to decrease aggregate sizes to less than 1 mm with agricultural equipment. If desorption is the limiting factor for degradation, the three-compartment model (Equation 2.16) can be used to predict the degradation. Examples will be shown in Chapter 5, 8 and 9 using rate constants measured under field conditions.

Especially during dewatering and ripening of the sediment, the presence of oxygen is the limiting factor for degradation. The relevant processes for the aeration in combination with the degradation processes as described before have been included in an aeration model to predict the results of landfarming during dewatering in order to evaluate different factors that can be influenced with the intention to improve the results. The model and model results are described in following sections.

2.5.1 Description of the aeration model

As shown, the presence of oxygen in developed soil aggregates depends on a large number of factors. Because the oxygen supply is most important during the start of landfarming of sediments, the model described is mainly focussed on the processes occurring during the dewatering phase of landfarming and includes:

- Formation and aeration through cracks as a result of shrinking (see 2.4.2).
- Size of aggregates as a function of moisture potential (see 2.4.4).
- Degradation of organic matter, rate of this degradation and requirement of oxygen (see 2.2.3).
- Oxygen present in aggregates (see 2.4.4).
- Variation of temperature during the year (see 2.3.5).
- Dependency of the activity of micro-organisms on temperature (see 2.3.5).

Because the amount of organic matter in sediment is much larger than the amount of contaminants and part of the organic matter in sediments is easily biodegradable, the requirement of oxygen for the degradation is set by the amount of degradable organic matter. It is assumed that the organic mater is degraded at the same rates as the organic contaminants. The three-compartment model (Equation 2.16) is used to calculate the degradation of organic matter. This assumption is based on results presented in the following chapters and the data presented in Table 2.5. Outputs of the model are the aerated fraction f_{ae} in the aggregates and the fractions of organic matter degraded present in the three compartments; all on different depths.

The model is used to describe the aeration in the sediment and degradation of fast degradable organic matter in Petroleum Harbour sediment, using a sediment layer of 1 meter. Subsidence by compaction and shrinking are taken into account (see 2.4.2). The treated layer is divided into 4 layers of 25 cm and the calculated results represent the situation in the middle of each layer. The model works with time steps of one month, which is small enough if several years of landfarming are considered. It is possible to use thinner layers and shorter time steps, but this should be done in combination with improved input data (Vermeulen, 2004). The purpose of the modelling applied was not to predict exactly what will happen on the landfarm, but to select the processes that have influence on the aeration and degradation and are applicable on a landfarm.

2.5.2 Results of the aeration model

The aeration model described in previous section has been run first (reference situation) using the following set of data (Table 2.15). Running the model using these conditions gave the aerated fraction and degradation curve as presented in Figure 2.13

Table 2.15 Used input for the landfarm aeration model (reference situation).

	Depends on	Used data
Crack area	Soil water potential	See Table 2.13
Air filled pore volume	Soil water potential	See Table 2.13
Equivalent radius	Crack area	See Figure 2.11
Temperature	Time	See Figure 2.7
Activity micro-organism	Temperature	See Figure 2.6
Oxygen consumption	Temperature, organic matter	See 2.2.3
Diffusion coefficient oxygen	temperature	See 2.3.5
Solubility of oxygen	temperature	relation presented by Rijtema *et al.*, 1999
Oxygen saturation in crack	Oxygen consumption and depth	Set at: 0-25 cm = 0.955 25-50 cm = 0.859 50-75 cm = 0.717 50-100 cm = 0.477
Organic matter	Amount and different degradable fractions (see Table 2.5)	41.51 g/kg fast degradable, $k = 3\ y^{-1}$ 35.89 g/kg slow degradable, $k = 0.35\ y^{-1}$ 21.62 g/kg very slow degradable, $k = 0.05\ y^{-1}$
Vegetation	Autonomic development	No vegetation in the first year. Roots in second year till 25 cm depth

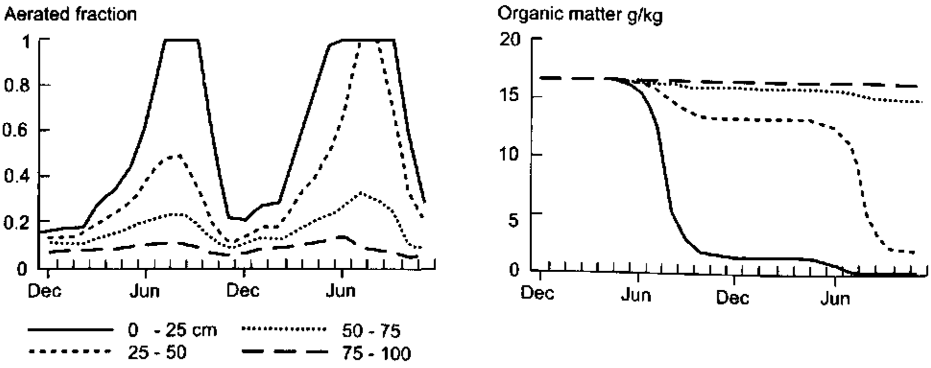


Figure 2.13 Aeration and degradation of fast degradable organic matter using the landfarm aeration model and input data as given in Table 2.15 (reference situation).

Figure 2.13 shows, that the aeration of the upper 25 cm is not a problem. In the second year also the second layer becomes aerobic. For the two lower layers the oxygen supply in the second year is not sufficient to achieve aeration. The aeration in the upper layer results in degradation of most of the fast degradable fraction in the first year. In the second layer a degradation period of more than 2 years is necessary due to slower aeration. The amount of degradation in the two lowest layers is very small.

If the organic matter is more easily degradable (set by a degradation rate constant of 10 y-1), it results (Figure 2.14) in a complete degradation in the upper 25 cm during the first summer. Because the easily degradable fraction is removed, a fully aerated layer is obtained earlier in next year. The higher oxygen consumption during degradation gives a lower aerated fraction in the lower layers In winter the aerated fraction drops to a lower value in the layers where the fast degradable fraction is still present. The degradability of PAHs can be improved by using oxidising agents (Cassidy et al., 2001) and surfactants (Volkering et al., 1995). In slurry systems these activities gave improved results. This calculation shows that these activities are not effective for landfarming of sediments, because on a landfarm oxygen is limited. Application of methods for increasing the availability for degradation conditions to occur should be combined with improvement in the aeration.

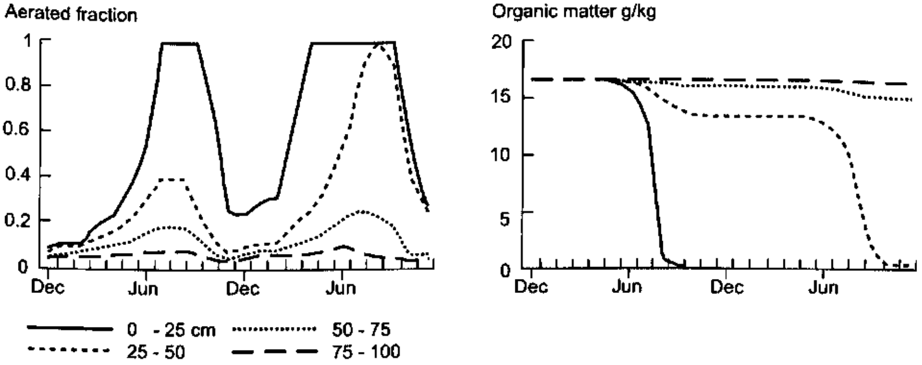


Figure 2.14 Aeration and degradation of fast degradable organic matter using the landfarm aeration model. Rate constant for fast degradable fraction 10 y^{-1}, other input data as given in Table 2.15.

The activity of micro-organism can be increased by using a higher temperature. This approach is often used by landfarming of terrestrial soils in halls in The Netherlands. Using the model, it is investigated if this can be successful for landfarming of sediments. The temperature is set at 16.8 °C; the highest temperature during the reference treatment. As shown in Figure 2.15 there is hardly any difference between the higher temperature and the reference situation. Only during the winter period the aerated fraction in the lowest three layers becomes smaller. From this figure it can be concluded that the activity of organisms is not limiting biodegradation, but it is the supply of oxygen. Increasing of the temperature can probably be effective after fully aerated sediment is obtained and the oxygen demand of the sediment is lower. The effect of higher temperature on degradation of contaminants after dewatering is addressed in Chapter 6.

Not taken into consideration is the increased evaporation at higher temperature. This has to occur at the surface of the landfarm. In winter condensation also will take place at the surface. High evaporation can only be achieved at high ventilation level and it is questionable if this can be achieved without high losses of energy in a landfarm. Cultivation as described below is probably more effective.

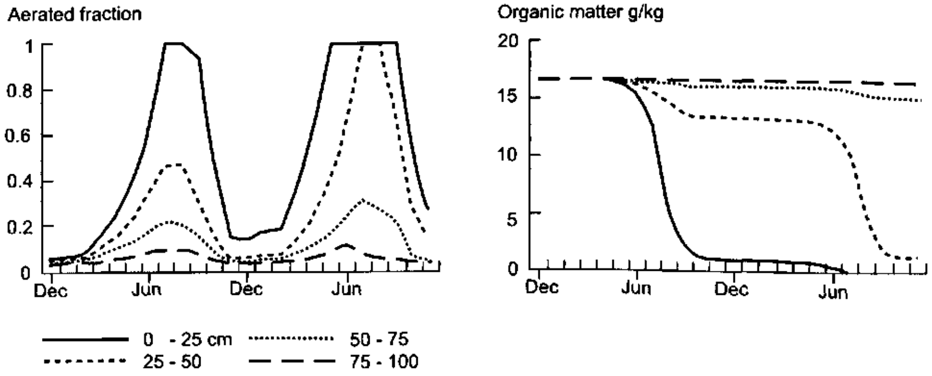


Figure 2.15 Aeration and degradation of fast degradable organic matter using the landfarm aeration model. Temperature at 16.8 °C, other input data as given in Table 2.15.

The demand for oxygen is reduced if the amount of oxygen consuming organic matter is lowered. This is simulated, by taken only one third of the original organic matter (Figure 2.16). This gave a high reduction of the oxygen need of the sediment. The upper two layers became more quickly aerated; the second layer also became quickly aerated in the first summer. Although the aeration in the lower layers improved, more time is still necessary to obtain a fully aerated soil. In the lower layers the sizes of the aggregates are still large because of the high moisture content (low soil water potential). Oxygen diffusion into these aggregates will be more important and this is a slow process compared to diffusion in cracks.

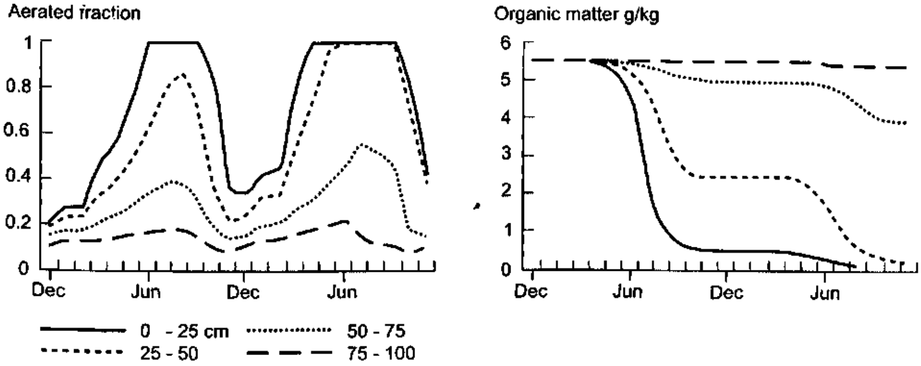


Figure 2.16 Aeration and degradation of fast degradable organic matter using the landfarm aeration model. One third of the original organic matter, other input data as given in Table 2.15.

Above model results shows that landfarming of a layer of 50 cm is possible if natural dewatering and ripening can be applied. The low aerated fraction on larger depths will be the limiting factor for landfarming of thicker layers. Improving the aeration by having complete oxygen saturation in all cracks (in the model this is achieved by setting the oxygen saturation on 1 at all depths) only slightly improved the results in the lowest layers. The maximum aerated fraction increased to 40 and 18 % in respectively layers between 50-75 cm and 75-100 cm. After 2 years respectively 14 and 2.4 % of the fast degradable organic matter (including fast degradable contaminants) was degraded on these depths. As mentioned before, at the highest depths the sizes of the aggregates are large and the supply of oxygen is the limiting factor.

The only way remaining to improve the aeration at larger depths is to decrease the moisture content, which can be obtained by an increase of the soil water potential. This can be achieved using intensive ploughing and cultivation during the first spring and summer, which will increase the evaporation of water. The frequency of ploughing must be high enough to prevent equilibration with the groundwater. All sediment parts will be at the surface during this year and complete (99%) degradation of the fast degradable organic matter (including fast degradable contaminants) in all layers can be assumed. After this period, the intensive treated sediment remains untreated and attains equilibrium again. Using this as input parameters, the aerated fractions (Figure 2.17) stay high, because the requirement of oxygen has become much lower. Only in the lowest layer is the oxygen supply still the limiting factor. This approach to the problem that includes intensive landfarming in the first spring and summer and passive landfarming in following years, a layer of 75 cm of Petroleum Harbour sediment can be treated on a landfarm. The degradation curve for this situation is not presented, because it is assumed that all organic matter was degraded in the first year. In this situation the degradation of the slow and very slow degradable fractions will start earlier at all depths.

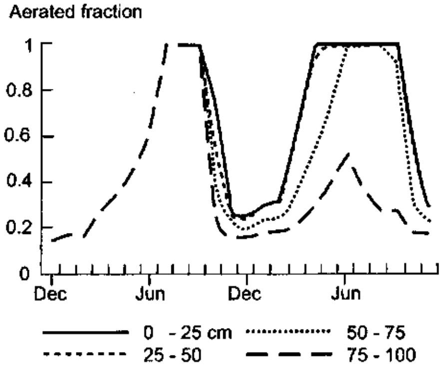


Figure 2.17 Aeration using the landfarm aeration model. The sediment is intensively treated until September and left further, other input data as given in Table 2.15.

Another way to increase the soil water potential is the use of vegetation having roots in the lower layers. Application of vegetation is already included in the model. In the reference situation, roots are present in the upper 25 cm in the second year. The effect of deeper rooting vegetation is given in Figure 2.18. In the first year vegetation is present with roots downward to a depth of 25 cm and roots develop to a depth of 50 cm in the second year. In this situation the second layer becomes aerated sooner compared to the reference situation and the aerated fraction in the layer under the rooted zone becomes larger. This gives an increase of the degradation of fast degradable organic matter and contaminants in this layer. Instead of 10% (reference situation) 38% is degraded. Degradation is less than in the intensive treated situation, but in 5-6 years complete degradation of the fast degradable fraction can be expected in this layer.

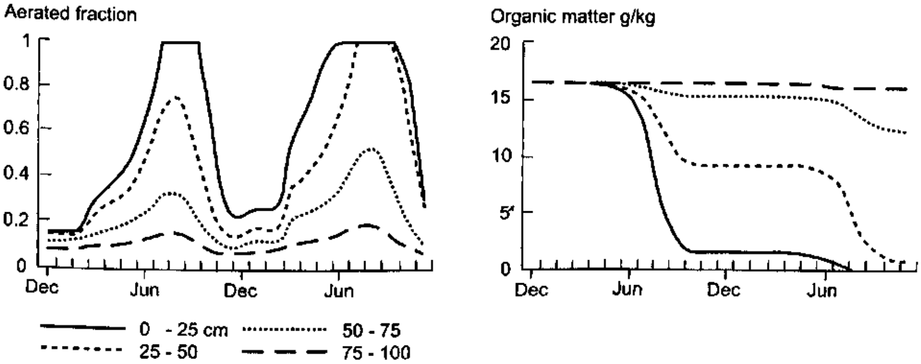


Figure 2.18 Aeration and degradation of fast degradable organic matter using the landfarm aeration model. Depth of roots 25 cm in the first year and 50 cm in the second year, other input data as given in Table 2.15.

2.6 Conclusions

To understand the amount of PAHs and mineral oil degraded during landfarming of sediment, it is necessary to focus on the three most important processes,

- Transport of the contaminant to a degrading organism.
- Presence of an active degrading organism.
- Presence of oxygen, necessary for aerobic degradation.

A contaminant is only degraded if the contaminant, the degrading organism and oxygen are present at the same place and at the same time. The presence can be expressed as the probability of finding each parameter in sufficient supply during the treatment time. If one of these is zero in the whole landfarm or part of the landfarm, then no degradation will occur and either no degradation or only partial degradation will be observed.

Contaminant

Diffusion of the contaminant from a site without an active organism to a site with this organism can be described with a first order process in combination with the existence of different adsorption sites. In the mathematical description of this diffusion the moisture contents and radius of the aggregate are very important parameters. The desorption rate constant is proportional to the square of the volumetric moisture content and inversely proportional to the square of the radius of the soil aggregate. Using the relations derived it has been shown that to achieve a high degradation rate the size of the developed soil aggregates must be reduced to sizes smaller than 1 mm, which is not realistic in a landfarm using normal agricultural equipment. At higher moisture content, higher degradation rates as result of faster desorption rates will be obtained. A high water content, however, reduces the possibility of diffusion of oxygen and the landfarm will become anaerobic. Increase of temperature has limited effect on the rate of the desorption process.

Contaminants in the water phase are not always present as individual solved molecules, but associated with dissolved organic matter. As a result, the differences in the partition coefficient of the individual contaminants become much smaller. If diffusion is the time limiting step for degradation, it is to be expected that the rate of degradation for individual PAHs becomes comparable.

Within a time frame of years, organic matter cannot be considered as a constant matrix. The rate of biodegradation of contaminants may also depend on the biodegradation of the organic matter, by which the adsorption sites are partly removed. Conversely, the organic matter may also change from a more rubber like form to a glassy form in which contaminants are more strongly absorbed (Luthy *et al.*, 1997).

Desorption processes, but also degradation of organic matter can be described using different desorbing or degrading fractions, expressed as fast, slow, and very slow. As mathematical description of the decrease of contaminant concentration as well as for desorption and degradation of organic matter a sum of first order decreases can be used.

Micro-organisms

Regarding the micro-organisms it is concluded that they can be found on several places in the treated sediment (the probability of finding an active micro-organism on these places is 1). The site must be large enough to contain an organism. Not al sites are large enough, so it will be necessary that the contaminant has to diffuse to the organism. Most bacteria are present in small pores <1.2 µm (Hassink, 1995) and the contaminant and oxygen have to diffuse to these pores.

Landfarming is a slow process, which means that the acclimation time can be ignored compared to the total process time. At the end of the landfarm period degradation will continue even below the threshold value. However, bacterial growth will stop resulting in a decreasing degrading bacterial population. The probability of finding an active organism will decrease resulting in an extra decrease of the degradation rate at lower concentration.

Oxygen

Sediments are anaerobic and after dredging they have to be transferred into an aerobic soil by dewatering and ripening. This gives physical changes in the sediment, which can be described by compaction and shrinking. The sediment becomes a soil with cracks and aggregates. The distribution and sizes of cracks and aggregates depends on the soil water potential. In the upper layer of landfarm and especially if vegetation is growing this potential is high, resulting in such a distribution that all aggregates will be aerated. At higher depths and closer to the ground water table the aggregates are larger and diffusion of oxygen into the aggregates becomes more difficult. The aggregates will only become aerobic if the amount of oxygen diffusing into the aggregate is at least equal or larger than the amount consumed by micro-organisms for degradation of organic matter. Moisture characteristics for soil can be derived from basic soil properties like clay and organic matter content and comparison with standard soils. Soil obtained after dewatering and ripening of sediments has a less compact structure compared to the standard soils.

Prediction of aeration and degradation

If the sediment is completely aerated, then biodegradation is limited by the desorption rate of the contaminant, or slow degradation of the organic matter. If the degradation rates are known, then the degradation curves can be predicted using a sum of first order decreases. In Chapter 4 and further, the rates are measured and predictions are made, which will show that this is a useful concept. In the first years of landfarming during dewatering and ripening, the oxygen supply is the most important limiting factor although also other factors may influence biodegradation. The effects of these factors are evaluated using an aeration model, which describes the aeration in different layers of the landfarm. Degradation of both contaminants and natural organic matter is only possible in the aerated fraction. In the model it is assumed that both organic matter and contaminants are present in compartments with the same degradation rate constants. The organic matter content is much higher and responsible for the oxygen demand.

In all calculations, aeration in the upper 25 cm goes fast and the fast degradable fraction of the organic matter is degraded within one year. Without activities on the landfarm, degradation of the organic matter in next 25 cm will occur in following year. In the lower layers the diffusion of oxygen is the limiting factor.

The effect of temperature on biological activity in the range 5°C to 25 °C is high. Increasing the temperature could increase the degradation rate, providing no other limitations were present. However the amount of fast degradable organic matter (including fast degradable contaminants) requires so much oxygen, that the diffusion of oxygen will limit the aeration. The model shows that higher temperature is not effective at the start of the landfarm. In addition, it will not be effective after degradation of the fast degradable organic matter, because in this phase of landfarming the desorption rate is limited. The desorption rate of contaminants is only slightly influenced by higher temperature (desorption is not included in the aeration model).

Increasing the availability of contaminants during dewatering is also not effective. This increases the oxygen consumption and the net result is nil, comparable with an increase in the temperature.

If the oxygen demand is decreased, aeration will also occur at higher depths. This can be achieved with a lower content of fast degradable organic matter in the original sediment, or by intensive treatment (cultivation) in the first year assuring that all fast degradable organic matter in the cultivated layer is degraded.

The aeration and resulting degradation can also be stimulated by reduction of the moisture content. This can be achieved by deep rooting vegetation. In the whole rooted layer a fully aerated structure will be achieved. This is easy to calculate with a model, but in practice it may take several years to obtain such deep rooting vegetation. A depth of approximately 25 cm below the rooted zone also remains aerobic. The total aerated depth with vegetation is comparable with the aerated depth after intensive treatment in the first year. The calculations are made for the Petroleum Harbour sediment (25% clay and 9% organic matter). Larger depths will be aerobic with more sandy, low organic sediments.

The calculations show that dry conditions stimulate the aeration and with optimal dewatering, large depths can be applied on a landfarm. Diffusion of the contaminant into the aggregates, however, is faster at wet conditions. These two demands are in contradiction and in the landfarming of sediments a compromise has to be found. Probably the Dutch climate conditions, wet in winter and dry in summer, is already a proper compromise. During winter diffusion is more optimal and during summer aeration is more optimal.

2.7 List of symbols

A_{cr} = crack area in m^2/m^2

ΔA_{cr} = increase crack area in m^2/m^2

A_{max} = maximum surface area of aggregate in m^2

b = ratio of water adsorbing capacity between organic material and clay minerals, the factor b generally is given the value 3.

[contaminant] = probability of finding the contaminant molecule on a place xyz, per unit of time

C/N = carbon/nitrogen ratio of the organic material

C_c = compressibility constant of the material in m/m

c = contaminant concentration in the aggregates in kg/m^3

c_o = sorbed contaminant concentration at $t=0$ in kg/kg

c_t = sorbed contaminant concentration at $t=t$ in kg/kg

c_{we}^{ox} = equilibrium oxygen concentration in water at the air/water boundary in kg/m3

D_w = contaminant diffusion coefficient in water in m^2/d

D_s^w = contaminant diffusion coefficient in soil/sediment pore water in m^2/d

D_{cr}^{ox} = oxygen diffusion coefficient in cracks in m^2/d

D_s^{ox} = diffusion coefficient of oxygen in pore water in m^2/d

D_{atm}^{ox} = oxygen diffusion coefficient in air in m^2/d

DOM = dissolved organic matter in kg/m^3

DOC = dissolved organic carbon in kg/m^3

d_{ag} = maximum diagonal hexagonal aggregate in m

d_{corr} = corrected value for diagonal hexagonal aggregate in m

d_{max} = maximum diameter of a water filled pore (m)

F_{fast} = fraction of contaminant in fast desorbing/degrading compartment

F_{slow} = fraction of contaminant in slow desorbing/degrading compartment

$F_{very\ slow}$ = fraction of contaminant in very slow desorbing/degrading compartment

fr_C = mass fraction C in organic material in kg/kg

fr_{cl} = mass fraction of clay in kg/kg

fr_{DOC} = mass fraction of organic carbon dissolved in water in kg/kg

fr_{linex} = fraction of linear extensibility

$fr_{linex,\ wp}$ = fraction of linear extensibility at wilting point

fr_N = mass fraction N in organic material in kg/kg

fr_{oc} = mass fraction of organic carbon in kg/kg

fr_{om} = mass fraction of organic matter in kg/kg

fr_{sa} = mass fraction of sand in kg/kg

g = magnitude of gravitational field strength in N/kg

ΔH = layer thickness without top load in m

J_{om} = fraction of organic material decomposed in the period considered in $kg/.m^2/d$

K_d = linear adsorption coefficient in m^3/kg

K_{oc} = partition coefficient between organic matter (expressed as organic carbon) and water

K_{oc}^{DOC} = partition coefficient between dissolved organic matter (expressed as organic carbon) and water

K_{ow} = octanol/water partition coefficient
k = first order kinetic rate coefficient in t^{-1}
k_{fast} = rate constant fast desorption/degradation in y^{-1}
k_{slow} = rate constant slow desorption/degradation in y^{-1}
$k_{very\ slow}$ = rate constant very slow desorption/degradation in y^{-1}
L_a = initial layer thickness of the dredged sediment on the landfarm in m
L_{cr} = length of cracks in m
ΔL_{cr} = increase length of cracks in m
[micro-organism] = probability of finding an active degrading micro-organism on place xyz, per unit of time
M = molar mass
m = shape factor for the aggregate structure, with
m = 0 for plate aggregates;
m = 1 for cylindrical aggregates;
m = 2 for spherical aggregates
n = soil ripening factor
n_c = number of contaminant molecule
[oxygen] = probability of finding oxygen on place xyz, per unit of time
R = correlation coefficient
r = distance from the surface to the centre of the aggregates in m
r_{eq} = equivalent radius assuming cylindrical aggregates in m
r_s = geometry factor
SOM = solid organic matter
S = water solubility in mole/dm^3
S_{ox} = oxygen demand of sediment in kg/m^3/d
S_{ox}^{C} = oxygen demand for carbon oxidation per day in kg/m^3/d
S_{ox}^{N} = oxygen demand for nitrification in kg/m^3/d
t = time in unit of time
$t_{1/2}$ = half life time in unit of time
V_{ag} = volume of aggregate in m^3
V_{cr} = crack volume in m^3
V_{dry} = volume of the aggregates in a dry state in m^3
V_r = moisture volume in the root zone in m^3/m^2
V_{sat} = volume of saturated soil aggregates in m^3
W_{cr} = width of cracks in m
x,y,z = co-ordinates in the volume considered

Z = final subsidence of the landfarm due to irreversible compaction in m

Z_{cr} = depth of brake point in subsoil moisture distribution in m

Z_r = thickness of the root zone in m

Z_{sat} = layer thickness at saturation in m

Z_θ = layer thickness at moisture content θ in m

ε = volume fraction of total pore space in the aggregate in m^3/m^3

η = tortuosity factor

θ = internal aggregate moisture content in m^3/m^3

θ_w = water content of the saturated sediment in kg/kg

θ_{sat} = moisture fraction of the saturated sediment in m^3/m^3

θ_r = moisture fraction in the root zone in m3/m3

ρ_s = specific weight of the sediment/soil in kg/m^3

ρ_{sa} = specific weight of sand in kg/m^3

ρ_{cl} = specific weight of clay in kg/m^3

ρ_{om} = specific weight of organic matter in kg/m^3

ρ_d = dry density of soil/sediment in kg/m^3

ρ_l = density of the liquid phase = 1000 kg/m^3

σ = surface tension of water in J/ m^2

ψ = soil water potential in mbar

3 Chemical measures of bioavailability

3.1 Introduction

Contaminants such as PAHs and mineral oil are biodegradable. In the short term (1-2 years on a landfarm), not all contaminants are degraded and a residual concentration is left. This lack of degradation is explained by limited bioavailability, which is a widely used concept. Bioavailability is one of the key factors in the selection of a remediation strategy (Rulkens *et al.*, 2003). The theories, explained in Chapter 2, provide a theoretical background for limited bioavailability. Without experimental confirmation, bioavailability will only remain a concept. Measured data that indicate the size of the bioavailable fraction and the kinetic parameters involved have to support (validate) the theories to explain slow biodegradation.

The ability to accurately determine the effects of contaminants on individual species, populations, communities and ecosystems is hampered by an uncertainty in the quantification of exposure of the individual species (Alexander *et al.*, 2003). This is also true for the prediction of biodegradability. This uncertainty has often resulted in a conservative approach in exposure assessment described in regulations that assume that the entire amount of a contaminant, present in a given soil or sediment, is available for uptake by possible receptors. Observations in laboratory and field studies have demonstrated that the responses of at-risk populations are not affected by the total concentration of a contaminant in the soil (Alexander, 2000). Instead, they are affected by only that fraction that is biologically available for that population at that time and soil condition. This is particularly true in soils that interact with contaminant molecules in such a way that the contaminant is not attainable anymore by the organism or is present in a not available form (sometimes referred to as sequestration or irreversible sorption).

The translation of information on bioavailability into acceptable evaluations of 'how clean is clean' (e.g., site-specific limits for regulating the extent to what concentration of a contaminant a soil has to be cleaned up) is essential for establishing realistic risk assessments and endpoints for remediation. Administrators, however, are still strongly focussed on total concentrations. These endpoints have already been in use for several decades and therefore are easier to handle. Chemical laboratories have supplied a large amount of 'total' data, which are also used for soil quality maps. Following a request from the field of risk assessment and standard setting, a discussion has started in the Netherlands in order to advise on the future role of biological availability in standard setting and risk assessment (Sijm *et al.*, 2002, Peijnenburg *et al.*, 2002).

In Europe, the Soil Communication Paper (EU, 2003a) has initiated a discussion on development of European soil strategy. In this discussion it was possible to include new developments, and the Task Group on Contamination concluded that (bio) availability has to be included in the new European policy: "policies for soil protection should be flexible and take aspects of (bio)availability into account, especially for immobile persistent chemicals (metals, PAHs). At least consensus on the concept of bioavailability should be part of new policy on soil protection" (EU, 2003b).

In those cases where a pollutant recently has been introduced to the system (such as in laboratory experiments or through the application of pesticides); there is chemical equilibrium between water and the solid phase. Effects can be predicted using partition coefficients that are measured in a specified soil or using a more general partition coefficient model (DiToro *et al.*, 1991) between organic matter and water (for organic contaminants). The equilibrium approach has been used and is still in use. This approach links the total concentration to effects of contaminants by calculating an available fraction. If the pollutant has already been present for a long time, it is not possible to explain effects from the total concentration and use of a partition coefficient (Beelen *et al.*, 2001). In different sediments and soils, measured partition coefficients may differ up to three orders of magnitude (Cornelissen and Kamerling, 2003). Assuming that the pore water concentration is responsible for effects on organisms, these effects can only be explained by introducing a bioavailable fraction of the contaminant.

The bioavailable fraction may differ from soil to soil and depend on soil characteristics and environmental conditions. Moreover, due to ageing, the binding of the contaminant to the soil may become stronger and effects on the environment consequently smaller. On the other hand, by natural or anthropogenic changing of soil factors (e.g., pH), contaminants may become more available.

Bioavailability can only become a practical tool when all risk assessors are using the same common concept and not their own specific one. For instance, a chemist can measure a chemical that he calls bioavailable, but as long as the chemical concentration has no relation to (biological) effects, it is meaningless. The same holds for a toxicologist who can measure an effect, but this effect has to be related to a chemical fraction of the total amount of the contaminant; the (bio)available fraction. By having a common framework on bioavailability, it will be possible to introduce workable (standard) methods that can be used in soil and site assessment. This chapter is a contribution to this discussion.

During the research for this thesis, bioavailability has been developed from a theoretical concept to a practical process, where bioavailability can be measured using complex methods and methods suitable for routine application in regulatory activities.

In this research, bioavailability has first been used to explain the sometimes limited aerobic degradation of PAHs and mineral oil. Later it has also been used to explain toxicological effects. Different ways of thinking about bioavailability in the different scientific areas are described in this chapter.

Although the full implications and mechanisms underlying bioavailability are still in development, the term has been used historically in agriculture and agronomy, for example, to describe the availability of nutrients and heavy metals to plants. In this chapter a summary of bioavailability for different applications is followed by an overview of possible chemical measures that could be used to establish the bioavailable fraction of organic contaminants. Experiments to develop chemical methods used in this study are described as part of this chapter. A chemical measure can only be meaningful when it is possible to relate the measured value with an effect. Finally, implementation and use of bioavailability in regulations is discussed.

3.2 Definition of bioavailability

Bioavailability is a concept for which no simple generic definition can be formulated. It is presented as a concept and always related to specific situations or to values measured by specific chemical extractions or bioassays. Consequently, bioavailability has to be defined conceptually as well as operationally. The National Research Council (NRC) Committee on Bioavailability of Contaminants in Soils and Sediments (NRC Committee, 2003) did not define bioavailability, but discussed 'Bioavailability Processes'. This discussion combines the conceptual and operational definition as used in this chapter.

3.2.1 Conceptual definition of bioavailability

A general definition of bioavailability is given in ISO/WD 11074: 'Bioavailability is the degree to which chemicals present in the soil matrix may be absorbed or metabolised by human or ecological receptors or are available for interaction with biological systems'. This definition is suitable as a conceptual definition, but has some limitations. The time factor is not clearly specified and it is not clear if there is a single degree of bioavailability or if it is dependent on the receptor or system. Users with different backgrounds have provided different, more specific definitions as to what they consider to be bioavailability. For practical purposes, more specific conceptual definitions have been derived, for example, as follows;

- bioavailability is the flux of contaminants to biota (Gary *et al.*, 1999).
- bioavailability is the amount of chemicals in the soil that are present in forms and amounts that plants or other organisms can take up during the time they are growing (Warrington and Skogley, 1997).

- bioavailability is the rate at which a chemical compound can be transported to the specified biological population (Shor and Kosson, 2000).

These definitions can be grouped into two categories (Wada, 2003), i.e., bioavailability defined in terms of flux or rate (mol/m^2/s) and bioavailability defined in terms of content (mol/kg). Theoretically, the content-based bioavailability is obtained by integrating the rate- or flux-based bioavailability over time. Practically, however, it is difficult to directly measure the rate of processes and the flux- or rate-based bioavailability is estimated from content-based bioavailability by dividing it by time. Therefore the content-based bioavailability is of primary importance from the experimental point of view.

It is interesting to ask colleagues with different backgrounds to describe the important aspects of bioavailability. The following aspects were mentioned[3]:

- Characteristics of the soil (organic matter, pore size distribution, structure).
- Type of organism, bacterivore vs. herbivore nematodes, man or wildlife, individual vs. population different ways of uptake.
- Properties of the contaminant, chemistry, speciation, mineral oil is not the same as heavy metals, mass transport.
- Time, life span of organisms, changing of soil properties, degradation.
- Bioavailability as a continuum, ranging from actual to potential.

It is impossible to incorporate all these aspects in a short definition. When reading a specific definition, it is always important to know the background of the author. Van Brummelen *et al.* (1998), as ecotoxicologists, prefer to use more general phrasing, analogous to the definition used in pharmacokinetic studies, described by Belfroid *et al.* (1996): "The fraction of the chemical (contaminant) present in soil/sediment and (interstitial) water which can potentially be taken up during the organism life-time onto the organism tissue". They suggest the best way to measure availability of PAHs is to determine the uptake rate parameters from kinetic studies. This is found to be quite laborious; also bioavailability is usually assessed from tissue residues. From an ecotoxicological point of view, measuring tissue residues seems logical, but it implicitly includes the opportunity of organisms to eliminate the contaminant and the possibility of organisms to regulate the uptake. For instance, PAHs can be bioavailable for micro-organisms, but will not be found in these organisms because they are biodegraded. PAHs can be found in fat tissue of worms but not in the tissue of worm-eating mice, because mice can eliminate PAHs. If the elimination processes are not taken into account, it will lead to an underestimation of bioavailability. Very important in their definition is the relationship with organisms. Bioavailability depends on the

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[3] With thanks to I.M.C.M. Rietjens, L.A. Bouwman, W.C. Ma, P.C.M. Frintrop, R.P.J.J. Rietra, G.F. Koopmans, W.J.G.M. Peijnenburg and R.C. Sims

organism; therefore there is not one type of degree of bioavailability, but bioavailability should always be combined with 'for' and the name of an organism or group of organisms. It is, therefore, necessary to distinguish between, for example, bioavailability for human beings, for plants and for micro-organisms.

In a stepwise approach suggested by Peijnenburg *et al.* (1997), it is possible to connect the target organism with the soil. This is based on the observation that for heavy metals, both abiotic (physico-chemical) processes and biotic (uptake and release) processes are, for the most part, related to the dissolved fraction. Therefore it is possible to subdivide availability into three phases:

- Physico-chemically driven desorption process.
- Physiologically driven uptake process from the water phase.
- Physiological/metabolic driven internal reallocation process, leading to degradation, to loading of a target organ, an accumulation organ, or release.

In this approach, the desorption process is described using distribution coefficients such as in an equilibrium evaluation. As shown in this thesis and by Beelen *et al.* (2001), the use of equilibrium is not possible for lipophylic organic contaminants. If equilibrium is replaced by interaction, in which interaction is properly described, this approach can also be used, as already described in this thesis in Chapter 2.

Cuypers (2001) also concluded that depending on the aim of the investigation, different definitions were used in the literature. From an environmental technology background related to bioremediation, he defined bioavailability as 'The ability of a contaminant to desorb to the aqueous phase, within the time-frame of an experiment, under infinite dilution conditions'. He assumed that all contaminants desorbed and present in the aqueous phase were available for biodegradation and were also degraded, which kept the concentration in the aqueous phase very low (infinite dilution).

From a chemical/transport point of view, availability is the amount per mass or volume unit that can desorb from soil or (suspended) sediment in a certain period of time under specific conditions. It can also be defined as the amount reversibly adsorbed to the soil again under realistic (temperature, moisture content) boundary conditions. Ecologists define bioavailability as the amount (or concentration) to which organisms are actually exposed, and that can be taken up, possibly causing an effect. Availability may also lead to biodegradation of the contaminant, which may be considered as a special type of effect. Including interaction with ground water, definitions are focussed on the amount present in the water phase and on the potential amount in equilibrium with the water phase of the soil. This is the amount roughly equivalent to the amount that can leach to lower soil horizons and ultimately to the ground water.

All these definitions include the time factor, which can be expressed as rate (1/t), life-time (t) and exposure (conc/t). There are barriers to transport in the soil, to organisms and within organisms to the target organ. These barriers to transport are soil or organism dependent and therefore constitute uncertainties. Combining all approaches the sequence as presented in Figure 3.1 is essential for the concept of availability.

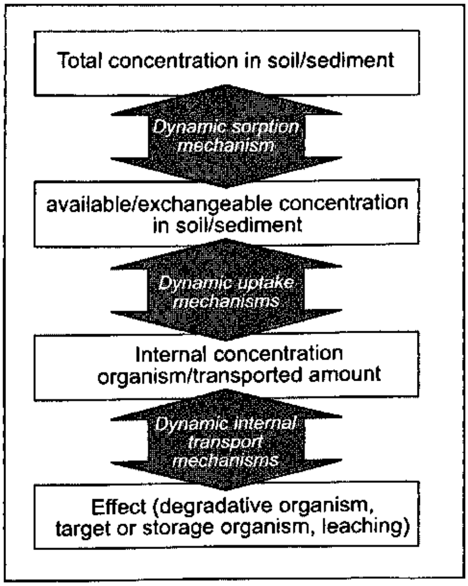

Figure 3.1 Pathways for contaminants adsorbed in soil to achieve an effect in the target organism.

Because availability depends on time, it is not a fixed fraction but should be divided into more fractions or described as a continuum. The simplest approach is to define an actual available fraction, a potential available fraction, and a non-available fraction. The potentially available fraction includes the actual available fraction but cannot exceed the total concentration. For establishing the potential bioavailability, it is important to define the total system: soil, including the organisms and environmental conditions that influence the fate of a contaminant in the soil or the activity of organisms. Considering an organism, a 'bio-influenced' zone can be defined, which is that part of the surrounding soil and pore water with which an organism interacts. Factors having influence on this zone are the possibility of an organism to produce exo-enzymes and other exudates or the possibility to influence the pH (thus affecting uptake by higher organisms). Consequently, the available concentration may have different values as illustrated in the following examples where two actual availabilities and four potential availabilities are distinguished:

- Organisms in bioassays such as *Vibrio fischeri* and *Daphnia magna* react on concentrations in the water (actual availability 1).

- To explain actual leaching, the pore water concentration can be used (actual availability 2). For potential leaching it is necessary to know the total amount that can desorb (potential availability 1).
- Micro-organisms can degrade the concentration in the pore water, but also the contaminant that is able to diffuse from small soil pores to the pore water during the bioremediation process (potential availability 2).
- Worms consume soil and may influence bioavailability due to physical and biochemical interactions with the organic and mineral soil constituents (potential availability 3).
- Small children also ingest small amounts of soil; due the human digestion system (also acid conditions) a strong interaction with the soil will occur and more may become available (potential availability 4).

From a soil scientific point of view, regardless of different uptake mechanisms, the formulation <u>1 minus the sequestered fraction</u> can approach the bioavailable fraction. It may be easier to measure the sequestered fraction instead of the available fraction for example, measuring PAHs present in large tar particles. "Sequestration can be defined as a process in which the environmental reactivity of a chemical is reduced by its complexation with other materials or its transfer or conversion to another phase or state in a manner that is not readily reversible. With respect to acceptable endpoints, sequestration must be defined in the context of a specific set of environmental receptors, relevant time and space scales, and route exposure" (Anderson *et al.*, 1999, cited by Ball *et al.*, 2000). When the extent of sequestration in any particular environmental scenario is better understood, it will support the concept of bioavailability. To accomplish this understanding, a reliable model is required to explain the processes of complexation, transfer and phase conversion (Ball *et al*, 2000).

For a definition that will be useful for different scientific disciplines, it may be convenient to use an illustration. In Figure 3.2, bioavailability is shown as used in this thesis. If there is contact of the contaminant with an organism, or contact takes place during the observation time, the contaminant is bioavailable. Organisms concerned are soil living organisms, from degrading micro-organisms to earthworms. In the soil particle, part of the contaminant is adsorbed on available sites and part on sites where it is not available for organisms, for example, in pores with a size smaller than the size of an organism. Available contaminants can easily move to the water phase, and come close to the organism (bioinfluenced zone). After passing the cell membrane, the contaminant will be transferred into the organism or biodegraded.

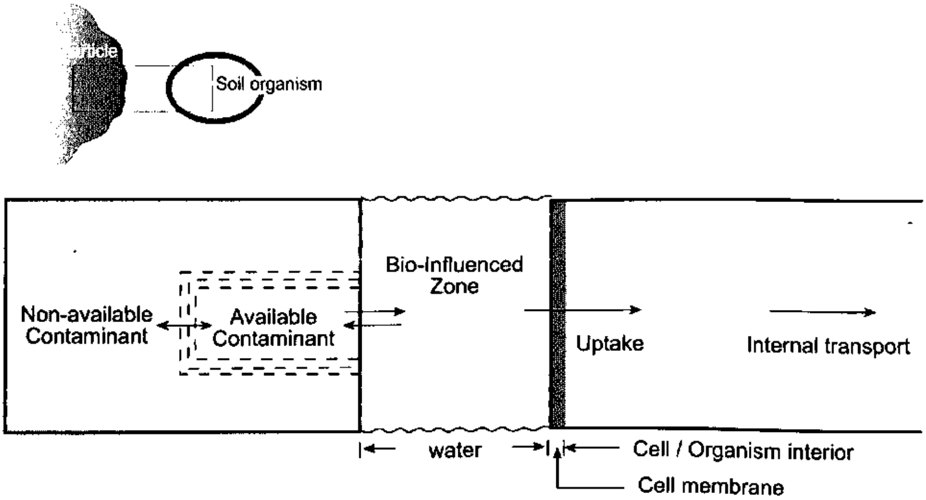

Figure 3.2 Conceptual diagram of the distribution of soil contaminants (i.e., available and non-available form), the bio-influenced zone that link soil contaminants to biological membranes and further transport in the organism. Adapted and modified from Alexander *et al.*, 2003.

It is important to differentiate between actual and potential availability. Actual means instantaneous uptake by or a direct effect on organisms. Measurement of the actual availability should therefore be focussed on that momentum and should not include a time dependent step. Bioavailability is the amount in the bioinfluenced zone plus the amount in instantaneous equilibrium with this zone (Figure 3.2). However, a time dependent step is always part of a method. An organism required time to take up a contaminant; and also chemical extraction procedures require a certain contact time. Depending on the organism and the method used, the amount of available contaminant will include a small or large part of the total amount (different dashed lines in Figure 3.2).

The potential bioavailability is larger than the actual. Potential includes the time factor and also a change in conditions of the contaminated soil or site. When conditions change, bioavailability changes too. This can be organism-related or soil-related. For example, the conditions in the stomach and in the intestines of children will cause a change in the potential bioavailability in consumed soil. In the soil, contaminants become gradually available due to diffusion from non-available to available sites, but may also become less available by diffusion to non-available sites (ageing). This is represented in Figure 3.2 with arrows between the grey and white areas in the soil. Soil degradation may reduce the capability of that soil for stable binding of a contaminant due to degradation of organic matter or decrease of pH. Degradation of organic matter especially reduces the capability to bind organic contaminants. New organic matter may incorporate organic contaminants and reduce bioavailability.

3.2.2 Operational definition of bioavailability

Based on the pore water concentration it is possible to explain effects like leaching, plant uptake and toxicological effects of heavy metals or of pesticides just after application using 'actual availability'. In those cases, 'available fraction' and 'pore water concentration' are equivalent. As a tool to measure the dissolved concentration, a weak extraction method having the same extraction power as pore water can be used.

The actual availability does not explain biodegradation of PAHs, or effects on soil consuming organisms such as worms (or small children), because other mechanisms and time frames are involved. More contaminant than present in the bio-influenced zone will pass through the cell membrane. For those purposes it is necessary to use the term 'potential' bioavailability. If the actual availability is defined as the concentration or activity in the pore water or the equivalent of that obtained in a weak extraction, the potential availability includes the adsorbed amount of the contaminant that can become available with time and through chemical processes. Several operational definitions can be used. Examples are:

- Biodegraded using a specified method.
- Uptake by specified plants.
- Uptake by a defined organism.

Regardless of the definition, the only direct way of measuring bioavailability is through the use of a target organism (Bioavailability$_{\text{target organism}}$). This leads to an operational definition such as: 'Bioavailability is the uptake (resulting in accumulation or an effect) of a component by a specified organism during a fixed period of time from the unit mass of soil involved'. However this type of testing procedure is not acceptable for use with higher organisms such as human beings. Therefore other organisms are often used to study potential effects. The number of organisms in the ecosystem is too numerous and test organisms that can be applied under laboratory conditions are often used as indices for the total ecosystem (Bioavailability$_{\text{bio}}$.)

If a crucial and rate limiting process involved in the uptake of a chemical by an organism or a group of organisms in a soil can be mimicked by a chemical process, Bioavailability$_{\text{target organism}}$ can be approximated by a chemical test, in which the chemical process is allowed to work in the soil for a specified period of time. In general, since the rate of the mimicking chemical process is not the same as that of actual overall processes, the time needed to measure the bioavailability by the chemical test (Bioavailability$_{\text{chem}}$) is not the same (usually less time is necessary) to that for Bioavailability$_{\text{bio}}$. Generally, an important condition required for Bioavailability$_{\text{chem}}$ or

$\text{Bioavailability}_{\text{bio}}$ is that it is a 1:1 function of $\text{Bioavailability}_{\text{target organism}}$ in statistical sense:

$$\text{Bioavailability}_{\text{target organism}} = f(\text{Bioavailability}_{\text{bio}}) = g(\text{Bioavailability}_{\text{chem}})$$

Where f and g represent some mathematical functions. The simplest case is that both f and g are linear functions, where $\text{Biovailability}_{\text{target organism}}$ is linearly correlated with $\text{Bioavailability}_{\text{bio}}$ and $\text{Bioavailability}_{\text{chem}}$.

$$\text{Bioavailability}_{\text{target organism}} = k_1\text{Bioavailability}_{\text{bio}} + C_1 = k_2\text{Bioavailability}_{\text{chem}} + C_2$$

Where k and C are constants and could be close to unity and zero, respectively, when the experimental conditions for biological tests and chemical tests are suitably adjusted.

Biological tests and chemical tests have to be considered as a tool to give indices of bioavailability for a target organism, both $\text{Bioavailability}_{\text{bio}}$ and $\text{Bioavailability}_{\text{chem}}$ should not be taken literally as 'bioavailability'.

3.2.3 Definition of bioavailability in this thesis

Because this thesis describes the biodegradation of PAHs and mineral oil, the conceptual definition of bioavailability is focussed onto biodegradation:

> *The amount of PAHs and mineral oil that can be transported (by diffusion or physical change of the adsorption site) to a site with a degrading micro-organism in a defined time period and that can enter the bio-influenced zone of this organism.*

This bioavailable amount will be biodegraded under aerobic conditions in that period, providing there are no other limiting conditions for degradation. Because the time period may vary, the bioavailable fraction is not a fixed amount. In addition, it is related to a specific situation. The research in this thesis concentrates on landfarming; therefore the operational definition is defined as:

> *The amount that is degraded aerobically on a landfarm in one year, under Dutch climate conditions.*

As a tool to predict the biodegradation, chemical measures are used, which extract a certain amount from the sediment. Because the mechanisms of these methods are understood this tool is in agreement with the conceptual definition as illustrated in Figure 3.3 (Harmsen *et al.*, 2003).

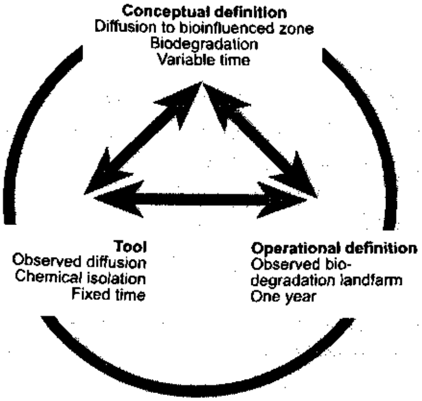

Figure 3.3 Used relations between conceptual and operational definition of bioavailability and the tool to estimate bioavailability.

With biodegradation, it is assumed that organisms degrade the contaminant and no negative effects remain. From an ecotoxicological point of view, biodegradation in the conceptual definition can be replaced by reaching a target organ in the organism or by achieving a negative effect in a part of an ecosystem. This will change also the operational definition and the tool. The tool can still be a chemical method, but also a bio-assay. As soon as the relation between the operational definition and the tool is understood, the operational definition may help to define an acceptable protection of the ecosystem. The value obtained with the tool can be used to predict if the protection level will be reached.

3.3 Present use of chemical methods for bioavailability

3.3.1 Nutrients

In the last half of the nineteenth century, agronomists and soil scientists began to search for chemical methods to determine the concentration of individual plant-available nutrients in agricultural soils. The impetus for this search was the need for recommended nutrient additions to achieve maximum crop yield. Mulder (1860) stated: *"Analysis for the composition of soil to establish the fertility is useless. Availability is the issue and not the amount present"*. Chemical methods were devised that reasonably predicted the bioavailability of inorganic ions necessary for plant development (Hissink, 1909; Mehlich *et al.*, 1935; de Vries and Dechering, 1938).

Chemical partial extraction methods are now commonly used to evaluate available levels of micro-nutrients in soils. Extraction methods have been optimised by correlating extraction results with response of susceptible crop species to the addition of fertilisers. An example of a routine soil test for plant-available (deficient vs. adequate) Zn, Cu, Fe, and Mn is the DTPA test of Lindsay and Norvell (1978). When any single extractant is used, results can be correlated well with the yield of one crop but not for various crops. Agricultural experience has identified the crops and the soils in particular regions for which an extraction method is applicable. Growers are advised to test their soils when they plan a crop on a soil that has not been fertilised with a nutrient for some years.

Soil water can be analysed directly to determine the actual amount of available phosphate. Certain extractants can be employed then to assess the availability of phosphorus with time (potential availability). It is possible to extract specific mineral fractions of phosphate, for example, phosphate present in amorphous (hydr)oxides, using an extraction with ammonium oxalate. In these minerals the potential available fraction of phosphate is incorporated. Total phosphorus concentration, combining available and non-available forms, is determined after complete digestion of a soil sample with strong acids (Pierzynski, 1998). In Europe 17 different methods are currently used to establish phosphate availability in relation to crop growth (Tunney *et al.*, 1997). Each method is calibrated (available concentration against plant uptake) and accepted by groups of users.

Due to the long tradition of using existing methods (more than 50 years for some methods), it has become increasingly difficult to implement new and improved methods, which requires new calibration, change in the existing framework, and acceptance by laboratories, advisors and farmers. An example is the extraction of soil with 0.01 M $CaCl_2$ to establish the availability of several nutrients instead of using different individual extraction procedures. In spite of scientific support (Houba *et al.*, 1990), and reduction in analytical costs, this method was not introduced in the Netherlands because of lack of calibration for all crops and soils, lack of finance to carry out the calibration, and therefore lack of acceptance by the users. Perhaps it was one step too far to replace a lot of methods by one single extraction method. At the present time, the extraction method with 0.01 M $CaCl_2$ is more critically evaluated and has obtained a mechanistic interpretation (Van Erp, 2002). Good results are obtained for magnesium and potassium and results of 0.01 M $CaCl_2$ can be related with conventional extractants. This increasing knowledge may support the introduction of this method, but also of other methods with the same principle (neutral salt extraction).

The influence of scientific publications is limited, as illustrated by the following example. Extraction with ammonium oxalate is used as an estimate for the potentially available fraction of phosphate. Adsorption methods (iron oxide impregnated papers or dialyses membranes filled with ferric oxide) are used to study in a more fundamental way the mobile fraction of phosphate (Freese *et al.*, 1995). Using this method, time is an important variable and by repeating the method with fresh adsorption material, a single soil sample should give the potential available fraction. Application, including replacement of the adsorbing paper during 66 days, allows for the extraction of 15 up to 70% of the ammonium oxalate extractable phosphate. Despite this large discrepancy between the two methods, there appears to be no cause for doubt on use of the established method (ammonium oxalate) for phosphate measurement as used in the agricultural field. The observed differences are still subject to scientific discussions, which will lead to a better understanding of the behaviour of phosphates in soil. A much longer period of time is required to transfer this knowledge on the availability of phosphate into tools for agricultural practise.

3.3.2 Heavy metals

Heavy metals in agriculture

Chemical tests of bioavailability are used in agriculture to assess toxicity in higher plants for elements including Zn, Cd, Ni, Cu, Co, Mn, and Al. Soils differ in the concentration of metals causing phytotoxicity. These differences are usually related to the ability of the soil to sorb or precipitate that element. Sorption ability of soils is commonly related to soil properties (characteristics) such as organic matter, clay content, levels of hydrous Fe and Mn oxides, and soil pH (which affects the sorption behaviour onto sorbing components). Consequently analysis of total concentration provides little useful information.

In general, it is recognised that metals in soil are either in the available fraction or are occluded in minerals. The 'labile pool' of an element is a good measure of the fraction that is potentially phytoavailable (Tiller, 1979). It is clear that some elements can be occluded within Fe or Mn oxides and become unavailable to plants, even to the extent that plants or animals grazing on those plants show deficiencies. It is known, for example, that Co is occluded within MnO_2, and Ni within Fe-oxides (Tiller *et al.*, 1969; McKenzie, 1970; Mclaren *et al.*, 1985; Bruemmmer, *et al.*, 1988). Cd in either oxide is poorly occluded, while Zn and Pb may be occluded to some extent (Ford *et al.*, 1997; Bruemmer *et al.* 1988).

Heavy metals in soils are mainly adsorbed on those components that determine the CEC (organic matter, clay and Fe- and Al-oxides) or are present as minerals such as carbonates. In sediments they may also be present as sulphides. Adsorption onto these minerals and soil components and or precipitation is more or less reversible. This, however, gives rise to different results when determining the bioavailable fraction. To predict the solubility or phytoavailability of the element at the existing soil pH, neutral salt extractions are commonly used rather than chelating agents or acids. There are different methods available that are variations on the same principle. Soil is shaken with water (or a dilute salt solution) and adjusted to a certain ionic strength (0.002 - 0.1). After equilibration, the water phase is separated by centrifugation, followed by filtration over 0.45 μm, and heavy metals are then measured. The dilute neutral salts (0.01 M $CaCl_2$ and 0.1 M NH_4NO_3) have shown to extract amounts of Zn, Cd, or Ni proportional to plant uptake (Sauerbeck and Hein, 1991; Prüe *et al.*, 1991). If the soil is wet enough, pore water can be obtained directly using special centrifuge tubes or porous cups that are placed in soils, pots or field sites. The measured concentration is the actual available fraction. As long as the amount in the soil is high compared to the amount in the water phase, and the methodology does not alter the soil properties, the ratio between water and soil will not be critical, and comparable results will be obtained measuring pore water or an extract.

Heavy metals in organisms

Smit *et al.* (1997) obtained a good correlation between the EC_{50} of the springtail *Folsomida candida* to both the $CaCl_2$-available and water-available extraction, both in freshly and long term polluted soil. During gut transfer in earthworms, the pH remained more or less neutral but organic matter was degraded, resulting in loss of binding sites. An extraction with buffered $CaCl_2$ (pH 7.2) gave a good correlation with the uptake of cadmium (Osté *et al.*, 2001).

Some types of higher organisms ingest soil, such as grazing cattle (sheep and cows) and small children. Their digestion system is more aggressive compared to soil living organisms (low pH in the stomach, a large variety of enzymes and longer residence times in the digestive tract). This may be responsible for a higher bioavailable fraction.

Because soil Pb comprises significant risks to children through the soil ingestion pathway, research has been conducted to identify methods to reduce the phytoavailability and bioavailability of Pb in soils. Feeding tests showed that soils differed appreciably in the relative bioavailability of the Pb they contained (Chaney and Ryan, 1994; Freeman *et al.*, 1992; Schoof *et al.*, 1996). The bioavailable fraction of Pb in soils can become reduced by both formation of very insoluble phosphate compounds (Ma *et al.*, 1993; Zhang *et al.*, 1998) and increased soil adsorption by phosphate and hydrous Fe oxide additions (Chaney and Ryan, 1994; Berti and Cunningham, 1997). Using these processes in remediation methods effectively reduced soil Pb bioavailability for pigs and rats (Chaney and Ryan, 1994; Brown *et al.*, 1997).

Chemical methods to evaluate the potential bioavailability of soil Pb have been under development since the 1990s. One of the early attempts used a bioavailability test developed for dietary Fe: measurement of dissolved Pb after 1 hr of stomach-like treatment of the soil, or after 1 hr of small intestine-like treatment of the soil. The measured Pb concentrations gave a good correlation with the bioavailable fraction to rats (Ruby, *et al.*, 1995). This method was further improved, simplified, and standardized as the Physiologically-Based Extraction Technique (PBET) (Ruby *et al.*, 1996).

A good correlation between the stomach phase extracted Pb and absorbed Pb (in blood or bone) was also observed in pig feeding studies suggesting that the extraction method could replace feeding studies (Medlin, 1997). The method has been examined further to simplify it as much as possible, and the original inclusion of enzymes, organic acids, and some other constituents were found to have no apparent effect on extraction of Pb. As long as the extraction fluid pH is in the order of 2.0-2.5, the simulated stomach phase extraction remains well correlated with absorption. Rood (2000), however, showed that the uptake is also influenced by the physiological status of the gastro-intestinal conditions. The gastric pH is expected to play a main role, and can be as low as 1 for fasting conditions and as high as 6 for fed conditions. Using her results, an acid extraction will give a worse case prediction of the uptake.

Questions remain about the reliability of both the pig and rat bioassays for estimating Pb risk to children consuming soil, as children cannot be tested directly. Adults have been tested, and weanling primates could be tested with different soils and treated soils to determine if remediation treatments reduce soil Pb bioavailability effectively, and whether different Pb-contaminated soils have different Pb risks due to different bioavailabilities.

Heavy metals in soil extracts

Leaching tests

Pore water is used to establish phytotoxicity of heavy metals and is also an important medium for leaching of heavy metals. The pH has been found to primarily explain the concentration in the water phase of cationic pollutants. In leaching tests different pH values are used (Van der Sloot *et al.*, 1997). By using different leaching tests, Van der Sloot (2002) was able to construct a figure showing the pH dependency of leaching of cadmium (Figure 3.4). The amount leached which is also an estimate of the available fraction, is low at neutral pH values and becomes increasingly larger in acidic environments. When children ingest the soil, the availability in the stomach is almost a factor 1000 higher than at neutral pH 8. A method using a complexing agent (EDTA) extracts the same amount as a solvent of about pH 2. This measuring point does not fit in the graph because the mechanism is different. Other important factors are the presence of complexing agents such as Dissolved Organic Carbon (DOC), chloride, and the redox potential. The increase in Figure 3.4 at higher pH can be explained by an increase of dissolved organic matter. Under anaerobic conditions such as those found in sediments, heavy metals may be present as very insoluble sulphides, and consequently their availability will be very low.

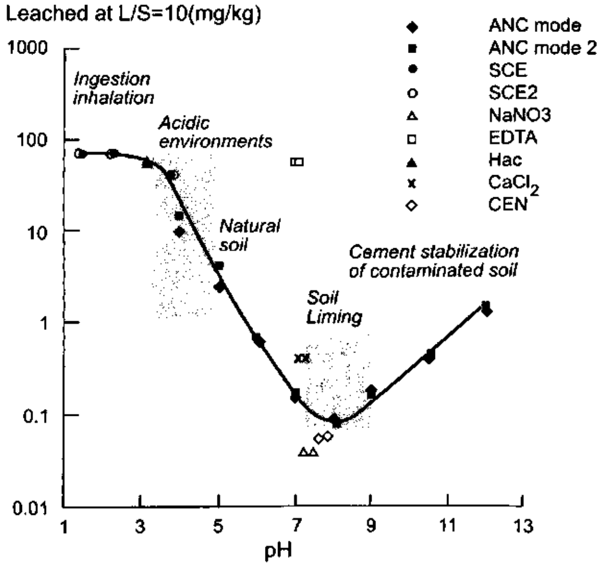

Figure 3.4 Leached amount of cadmium from a cadmium-contaminated soil as function of the pH. Different leaching/extraction tests have been used in a method-harmonisation project. Adapted from Van der Sloot (2002).

Modelling of availability

It is possible to calculate the water-soluble part from the potential available fraction (mild solvent extraction) using transfer functions (Reinds *et al.*, 1995, De Vries *et al.*, 2002). Knowing that dissolved concentration is the driving force for plant uptake (at least for the supply to the plant root), the uptake can also be predicted from the pore water concentration. A transfer function contains parameters that explain the distribution between the dissolved fraction and the solid phase. The most important parameters are the soil characteristics pH, clay content and the content of solid organic matter (*SOM*). A further improvement is the introduction of water characteristics like Ca^{2+} and *DOC* (dissolved organic carbon). Examples of a transfer function are given below. Reliable transfer functions for cadmium and zinc are available (Römkens *et al.*, 2004). Those for copper and lead are less reliable as shown by the smaller correlation coefficient R^2 (Table 3.1).). The best relationship in arable soils between heavy metal content and actual available amount in the water phase is not obtained by using the total amount obtained with an Aqua Regia digestion, but by using an extraction with dilute acid (0.43 M HNO_3). The amount extracted with diluted acid can be considered as the potentially available fraction. This is in agreement with the maximum leachable fraction as presented in Figure 3.4. Values in the transfer functions (Table 3.1) are obtained by multiple linear regressions of measured data (Römkens *et al.*, 2004).

$$\mathrm{Log}[Q_{soil}/\{c_{solution}\}^{n}] = INT + a \cdot \log[SOM] + b \cdot \log[clay] - c \cdot pH + d[DOC]$$

where:

$c_{solution}$ = actual available in water phase
Q_{soil} = concentration extractable using 0.43 M HNO_3
INT = Intercept obtained by multiple linear regression
$[SOM]$ = solid organic matter content (%)
$[DOC]$ = dissolved organic carbon (mg/l)
$[clay]$ = clay content (%)
$a, b, c,$ = coefficient obtained by multiple linear regression
n = non-linearity term

Table 3.1 Values for *INT*, *a*, *b*, *c*, *d* and *n* in transfer functions.

Metal	*INT*	*a* (*SOM*)	*b* (*Clay*)	*c* (*pH*)	*d* (*DOC*)	*n*.	R^2
Cd	-4.75	0.61	0.26	0.29	-0.05	0.54	0.80
Cu	-2.61	0.60	0.12	0.23	-0.27	0.59	0.65
Pb	-2.38	0.95	0.22	0.07	-0.23	0.73	0.59
Zn	-4.23	0.47	0.43	0.37	-0.14	0.75	0.82

Comparable functions are available to predict the amount of heavy metals in different crops grown on contaminated fields (van Wezel *et al.*, 2003) and for the amount in total body tissues of earthworms in contaminated fields (Ma, 2004).

Different availabilities for heavy metals

As discussed previously, there are different degrees and forms of availability. The size of the available fraction depends not only on generic soil/sediment conditions (chemistry), but also on uptake pathways. The available fraction in the stomach after ingestion of soil is higher compared to the availability for plant uptake. Results of different extraction procedures, with different extraction strengths, correlate with different measured effects. It should also be realised that the same measured available fraction may lead to different uptake due to internal regulation in the organism. Plants have exclusion mechanisms to prevent uptake, but specific plant species function as hyper-accumulators of heavy metals.

There are at least 3 different levels of heavy metal concentration, actual and potential available and the total concentration, as illustrated in Figure 3.5. The heavy metal concentrations in these levels have to be extracted using different extraction methods; they also cause different effects. They can be extracted with respectively a neutral solvent, a mild extraction and aqua regia (total minus silica bounded heavy metals). The increasing extraction power of these methods is presented with an arrow. This larger measured chemical availability can be correlated with the bioavailability for organisms and also with a higher extraction rigor, or with the possibility for leaching, as represented with the second arrow. Only if the extraction procedure and the uptake by the organism are measures for the same amount, the chemical extraction procedure can be correlated with the effect in the organism.

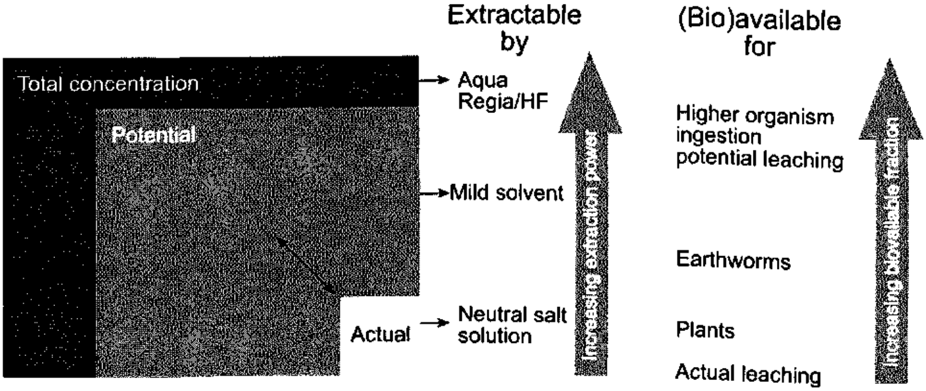

Figure 3.5 Distribution of heavy metals in sediment or soil over different available fractions, using different extraction procedures, and the availability for organisms and leaching.

3.4 Requirements for chemical methods for measurement of bioavailability of organic contaminants

Similar to the situation for nutrients and heavy metals, results of chemical methods or assays for measurement of bioavailability of organic contaminants in soils and sediments must be correlated with the results of biological assays. Although the measurement of availability of organic contaminants is a newer field of research, some of the chemical procedures that have been proposed or under development are promising. Within the chemical methods, two approaches can be distinguished:

- A kinetic approach, in which a fraction and a rate are considered. There is no known relation with the total concentration, except that the available concentration is smaller than the total concentration.
- An approach based on chemical equilibrium, in which the availability is used to correct the values derived from application of the equilibrium partition theory (for example, the approach described by Krauss and Wilcke (2000-a)).

The second approach may result in a circular definition of total concentration. We know that the total concentration in an individual soil is insufficient to predict effects; therefore the biological available fraction has to be measured. With an individual soil sample, bioavailability can be used to correct the K_{oc}-value (partition coefficient of a contaminant between soil and water). If enough samples over a large concentration range have been measured, there certainly will be a correlation between this correction and the total concentration within one order of magnitude. In other words, the available fraction is within 10-100% of the total concentration. If such a fit is used to replace the total concentration, a new 'total' concentration is created but also this value formally has no relation with biological effects in specific situations.

3.4.1 Measurement of total concentration of organic contaminants

Measurement of the bioavailable fraction should only measure the available fraction, which is part of the total concentration. Measurement of the total concentration of organic contaminants is not as simple as it seems. Unlike measurements of heavy metals in soils, it is not possible to use aggressive chemicals that destroy the soil matrix and leave the metals in solution. These types of methods would also destroy the organic contaminant to be measured. In addition, methods for heavy metals can be compared and validated with nuclear activation methods that are matrix independent and measure the real total concentration. For organic contaminants, extraction methods have to be used that are based on a distribution of the contaminant between the extractant and the soil matrix. There is no reference method available that can assure that the total concentration has been measured. In the following section, the factors that are important for the extraction of organic contaminants from soil are discussed.

Presence of organic compounds in soil

Organic contaminants present in soils and sediments can be the result of direct or diffuse pollution. The source of pollution may strongly affect where contaminants are present on the site and in the soil samples to be analysed. Direct pollution, as in a lot of heavily polluted industrial sites, may result in presence of the neat contamination (e.g. tar-like particles or liquids), which even can be visually recognisable. In diffusely polluted areas, the contaminants are more equally distributed and are mostly not visually recognisable; their presence can be described as molecules adsorbed on or absorbed in the soil. The contaminants can be introduced through air pollution, water pollution, agricultural practices or long-term use of slightly polluted sludges. Contaminants therefore can be present in soil and sediments in different physico-chemical forms, as shown in Figure 3.6 (Rulkens, 1992). In this figure, presence of the contaminant is divided into particles, liquid film, adsorbed on or absorbed in soil aggregates, or present in large as well as in small pores.

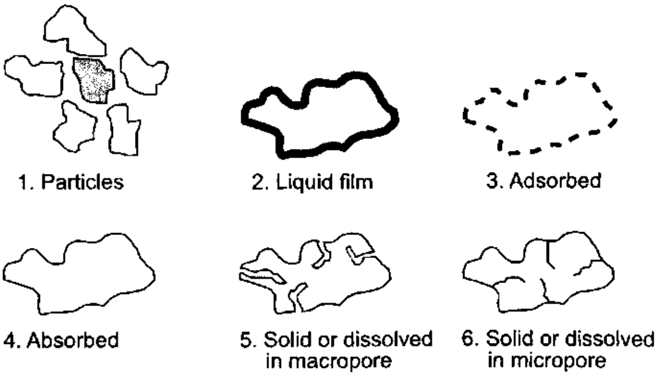

Figure 3.6 Appearance of contaminants in soil or sediment. Adapted from Rulkens, (1992).

It is important to realise that the scale in soil varies from tenths of microns in case of absorption to tenths of millimetres in case of particles and films. The organic compounds are bound to the soil with different strengths, and are preferentially bound to soil organic matter, because most compounds are lipophylic. If the soil is homogenous, this binding can be described with chemical equilibrium formulae using distribution coefficients. From an analytical point of view, the contaminant can then be extracted with a solvent with a strong attraction for this contaminant. Soil, however, is not a homogenous material. On a small scale, the binding to the soil can be described as a normal chemical or physical interaction. The larger scale interactions of contaminants in soil aggregates with the surrounding liquid phase are more complex. For instance, if an organic compound is accessible to an extractant solvent, the contaminant will be extractable if it has preference for the solvent and dissolves in the solvent. If the same organic compound is absorbed in the soil organic matter or in a micro-pore, it is more difficult for the extractant to reach the contaminant than to dissolve the contaminant. Therefore, the extractability in soil is not only a function of the preference of the compound for the solvent, but also of accessibility of the soil matrix. This results in a range from compounds that are easily extractable (for example, compounds present as separate droplets or films or adsorbed on the surface of soil aggregates) to very difficultly extractable compounds that are absorbed in very small soil pores or within organic matter. In Figure 3.7, extractability is illustrated as a hypothetical distribution curve. Only a solvent that can reach all sites in the soil and that is strong enough to dissolve the compound will extract everything (represented as the total surface) from the soil matrix. If the accessibility of the contaminant is low or if the contaminant is strongly bound to the soil matrix, less will be extracted: the appearances 4 and 6 in Figure 3.6 are present in the right part of Figure 3.7. The amount of the contaminant under the right part of the curve will not be extracted using weaker extractants. Because the organic contaminants that are the subject of this thesis are lipophylic and strongly associated with organic matter, the amount of the compounds that is direct available (extreme left part under the curve) is very low.

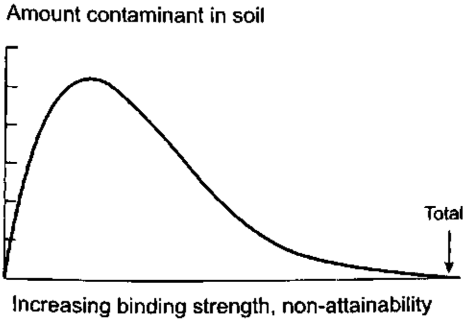

Figure 3.7 Distribution of a contaminant over sites with different accessibility and binding strength. Adapted from Harmsen and Frintrop (2003).

To isolate or extract a compound from the soil matrix, the following procedure steps are necessary (Harmsen and Frintrop, 2003):

1. The extractant has to reach the compound (accessibility).
2. The extractant has to release the compound (dissolving).
3. The soil matrix has to be separated from the released compound.

In many extraction procedures, the emphasis was on step 2, for good solvents were also considered to be good extractants. Steps 1 and 3 are not determined by the properties of the organic compound, but by the soil matrix. The properties of organic contaminants differ from the properties of the soil. It should also be understood that contaminants present in sediments and soils are not adsorbed to the most attractive adsorption sites, but that adsorption sites are determined more by the fact that the contaminants have less attraction to their original environmental matrices (water and air).

For most organic contaminants, non-polar solvents such as petroleum ether and toluene are very good solvents. These solvents, however, cannot reach every micro-pore in the soil. They leave the soil aggregates intact and will not mix with residual water present in small pores. Such solvents may give good results when the contaminant is adsorbed on the surface of soil particles or present as solid particles or as film, as mostly is the case with fresh contaminants. These solvents also give good results with recovery experiments such as those used during method development, because it is easy to extract freshly added contaminants. In aged polluted soil, however, the contaminant molecules do not stay on the surface; redistribution occurs with time, resulting in diffusion to and adsorption onto sites (micro-pores) that are not accessible by these types of solvents. The accessibility can be increased by using a more polar solvent that disintegrates the soil aggregates (such as acetone) or by adding extra energy, i.e. through using a higher temperature, higher pressure, longer extraction time, or ultrasonic or microwave radiation.

Extraction methods for measuring the total concentration

When developing a new method and comparing it with other methods, it is not sufficient to measure just recovery percentages. Added compounds are easily accessible to extractants and may even be extracted using a poor method. Certified Reference Materials (CRMs), which are materials with a known (certified) concentration of contaminant, are available for a variety of classes of compounds. These materials can be used to evaluate an extraction method. A check of the extraction efficiency can also be achieved by extracting the residual soil with other exhaustive procedures such as Soxhlet extractions. If the extra amount of the contaminant measured is negligible compared to the amount obtained in the first extraction, it may be concluded that the first one is sufficient.

Soxhlet

Soxhlet has been developed for the determination of macro compounds, e.g. lipid content in food. It is a more or less continuous extraction procedure and it is regarded as an exhaustive extraction. The idea of an exhaustive extraction is very appealing for both macro and micro pollutants. Therefore 'overnight' extractions, i.e., using extraction times of 14 to 16 hours, are quite common with Soxhlet extraction. For micro-pollutants, such long extraction times may have some negative effects. This is caused by the non-specificity of any extraction procedure. Suppose that after n- cycles, 70% of the organic contaminant (analyte) and 10% of more polar, but in the further measurement, interfering compounds, have been extracted. The ratio between wanted and unwanted compounds is 7. After 2n cycles the recovery of the analyte has increased to 91% (70 + 70/100 *(100-70)) but at the same time the interferences have increased to 19% (10 + 10/100 *(100-10)). The ratio between wanted and unwanted has decreased to 3.7. It is clear that 'infinite' extraction will end in an extract with quite a high content of unwanted substances. For the extraction of micro-pollutants, the power of the exhaustive extraction is at the same time a problem.

Soxhlet extraction does not apply any additional forces. The sample is soaked in the extraction liquid, and with each cycle this liquid is supposed to drain completely from the sample. This procedure requires that the grain size of particles in the sample has to be small in order to have sufficient accessibility for the extraction liquid. However, the sample should not become too tightly packed because in that case, only the outer surface will be extracted. Accessibility is also improved by using a water miscible solvent or by removing the water by drying the sample before extraction.

Shaking (agitation) procedure

Extraction by shaking is quite common in standard water analysis procedures. It is also when the water sample contains appreciable amounts of suspended solids. Extraction by shaking has the advantage of both a proper mixing of the extraction liquid and the sample and the enhancement of accessibility by the applied mechanical forces. These benefits may also be obtained by shaking soil samples with an appropriate extraction liquid. For field moist soil samples the extraction liquid has to be sufficiently mixable with water, because the mechanical forces itself are insufficient to provide accessibility for non-water mixable solvents like petroleum ether, pentane and hexane. Acetone and methanol are very well suitable to overcome the water barrier, for they will break up the soil aggregates. The polarity of acetone or methanol is rather high, making them less suitable as a solvent for non-polar compounds. Adding a less polar solvent that is mixable with acetone or methanol will overcome this problem. This means that a two stage extraction is performed; the first is a short (10 minutes) shaking with acetone or methanol only and after that a longer period (2 hours) of shaking with the mixture of acetone or methanol and petroleum ether, pentane or hexane.

Under normal conditions the acetone will be removed from the extract by shaking the total extract with a large amount of water. It is this step that governs the final amount of extracted compounds that will be measured. The removal of the acetone will also imply a removal of other more polar compounds (K_{ow} < approx.3). Therefore, these compounds cannot be measured using the above extraction procedure. For the extraction of non-polar compounds, the removal of the acetone and other polar compounds may be regarded as a first clean-up of the extract.

Examples of the shaking procedure can be found in several ISO-standards for the determination of organic micro-pollutants in soil, such as PAH, OCB and PCB, mineral oil, herbicides (respectively ISO 13877, ISO 10382, ISO/DIS 16703 and ISO/FDIS 11264).

Accelerated solvent extraction and super critical fluid extraction

Accelerated solvent extraction (ASE) uses higher temperature and pressure, resulting in a more effective and shorter extraction process. As long as accessibility for the extractant is high enough, ASE will give high recoveries. ASE is a promising method for extraction of organic contaminants in soil. The extra input of energy by increasing the temperature and pressure makes it possible to reduce extraction times. However, if barriers for the solvent exist, such as the presence of water or large soil aggregates, ASE may also be ineffective. The first barrier can be overcome by using a water mixable solvent, by adding methanol to a non-polar solvent, or by chemically drying the sample. The presence of large soil aggregates may limit the use of ASE, because mechanical shaking in combination with an appropriate solvent is necessary to break these aggregates.

Super critical fluid extraction (SFE) broadens the possible use of 'solvents'. Using super critical carbon dioxide has the advantage that the final extract is automatically concentrated to dryness. The polarity of super critical carbon dioxide is rather low, therefore, small amounts of methanol are added as a 'modifier' to increase the polarity of the extractant. The solvents also have a large penetrating power because of their low viscosity. The development of ASE has reduced the interest in SFE due to the more versatile applicability of ASE.

3.4.2 Established methods for measurement of bioavailability of organic contaminants

Pesticides are a special group of organics that are used to support the growth of crops. Pesticide bioavailability has been an area of significant interest, not only from an environmental point of view, but also to improve the effectivity of a pesticide after application. In particular, much work has been done to develop methods to predict application rates and the potential for pesticide carry-over to the next growing season. Numerous types of assays have been evaluated to determine whether the extractions correlate well with phytotoxicity. Results demonstrated that plant damage was poorly correlated with total extractable compound, particularly in soils containing aged pesticides. In response, biological assays were employed, which were predictive but more expensive than chemical analyses. Eventually many of these bioassays have been replaced by pore water analysis (analogous to techniques developed for sediments (Adams *et al.*, 1985) and reviewed by DiToro *et al.*, 1991 and Boesten, 1993) that were able to correlate soil herbicide concentration with plant damage. The pore water analysis method involves centrifugation of a soil sample to obtain the water that is trapped within the soil matrix. The soil water is then subjected to chemical analysis. Results of such experiments indicated that for some materials that are acutely toxic (e.g., an herbicide for a sensitive plant or an insecticide for a target soil insect), pore water analysis provides a good approximation of bioavailability (Houx and Aben, 1993; Ronday *et al.*, 1997). These chemical tests correlated well with plant injury and allowed the agriculture industry to decrease its reliance on bioassays.

There are, however, large differences between pesticides and organic contaminants like PAHs and mineral oil. First the water solubility of modern pesticides is much higher, which makes it easier to analyse a pore water sample (i.e., higher concentration of the pesticides are present in the pore water). Second, pesticides are freshly added and the amount adsorbed in non-accessible sites will be smaller. Results obtained for pesticides are therefore not directly applicable to contaminants such as PAHs.

3.4.3 Promising new chemical methods for measurement of bioavailability of organic contaminants

Recently some new chemical methods have been described that are empirically based. Some are based upon attempts to mimic conditions of biological uptake or processes in the soil. Not all promising analytical results have yet been studied with appropriate bioassays. The following methods are described further:

- Water Based Extractions, extracting the pore water or using some extra extraction power by adding molecules or a solid phase with extraction power able to 'adsorb' the available contaminant.
- Solvent Based Extractions with single solvents or multiple extractions.
- Use of the characteristics of different forms of organic matter to distinguish adsorption sites of different strength.
- Thermal desorption to remove the more available contaminants.
- Techniques derived from molecular biology and the use of 'engineered' organisms.

Water Based Extractions

Extraction of pore water

Determination of contaminants present in water in soil pores have been described for nutrients and heavy metals (Section 3.3) and for pesticides (Section 3.4.2). Johnson and Weber (2001) used heated and superheated water to measure long term desorption of phenanthrene. The Arrhenius equation was used to extrapolate the experimental results measured at temperatures between 75 and 150 °C to an ambient temperature of 25 °C.

Using pore water analyses, the measured availability is limited by the solubility in water. As long as the distribution between the solid soil and the water phase can be described by an adsorption curve (assuming equilibrium between the solid and the liquid phase), this type of measurement can be used to describe direct effects, as has been done for pesticides. Leaching tests (van der Sloot *et al.*, 1997) are a further development of the water extraction procedure to predict leaching. An important difficulty with a water extract is the separation of the water phase from the soil matrix. The pore water can be obtained by centrifugation of soil samples or by using porous tubes and cups in equilibrium with the soil. It is important that the contaminant to be analysed does not react with the equipment being used for the analysis. No interaction can be assured for relatively soluble compounds such as modern pesticides, but not for low soluble and non-polar PAHs. Losses of PAHs by adsorption have been observed, even on stainless steel (unpublished results). Use of filters responsible for losses due to adsorption can be overcome by the use of centrifugation. If a clear extract without solid particles can be obtained, the result will be a reliable estimate of the pore water concentration. If this is not possible, it must be realised that the concentration of a pollutant in the solid particle is mostly much higher compared to that in the water phase. The measured result will be an over estimate of the pore water concentration.

It should also be kept in mind that, with time, the solubility of contaminants can become too small to measure, in addition to the analytical problems encountered, such as adsorption onto equipment. Therefore, for practical purposes, there is a limit to the application of tests where a dissolved water phase is necessary for measurement. The use of molecular and solid phase extraction described in following paragraphs as part of the experimental set up may overcome these problems.

Solid-phase extractions

Solid-phase extractions (SPE) offer considerable promise to establish the bioavailability of non-polar contaminants such as PAHs. They act as an 'infinite' sink for the contaminants. The low soluble organic contaminant is adsorbed by the solid phase and keeps the pore water concentration very low. Due to this gradient all the available PAHs will diffuse to the water phase and will be adsorbed on the solid phase. After a set period the available contaminant is transferred from the soil to the solid phase. The solid-phase extractants used are Tenax TA beads, XAD-resins and C18 membranes. Main differences in SPE procedures are agitation procedures where the solid phase is present in excess (Tenax and XAD) and procedures where a membrane is placed in situ and local availability is measured.

Good correlations are shown between DDT, DDE, DDD, and PAHs uptake by *Eisenia foetida* from a range of soils and the quantity sorbed by solid phase extraction (Morrison *et al.*, 1999; Morrison *et al.*, 2000; Tang and Alexander, 1998). Besides prediction of degradation, Tenax beads have also been used to measure the desorption kinetics of some chlorobenzenes, polychlorinated biphenyls (PCBs) and PAHs (Cornelissen *et al.*, 1997 and 1998). XAD-resins used in a similar procedure have also been shown to be applicable for measurement of desorption of PAHs (Northcott and Jones, 2001).

Instead of beads, disks or needles have also been used to measure the availability of organic contaminants for organisms in aqueous systems. These devices are used as samplers, also called passive samplers, and take up contaminants from the water phase. Several systems have been investigated:

- Semipermeable Membrane Devices (SPMD) made of low density polyethylene (Huckins *et al.*, 1990; Booy *et al.*, 2000).
- Solid Phase Microextraction (SPME) with octadecyl, but also other adsorbent materials (Arthur and Pawliszyn, 1990; Mayer *et al.*, 2000; Verbruggen *et al.*, 2000).
- Stirr Barr Sorptive Extraction with polydimethylsiloxane (Baltussen *et al.*, 1999).

SPME can also be applied to sediments and soil. It has been used to simulate the uptake of contaminants by organisms by placing the device in the sediment or soil, and analysing it, after removal of the adherent water, by thermal desorption and gas chromatographic analyses. By using long extraction times (15 days), results can be correlated with the soil-to-biota accumulation (BSAFs) of earthworms (Krauss and Wilcke, 2001-b). Leslie (2003) used shorter times (4 days) to predict the effects of contaminants on aquatic organisms (adult oligochaete worms and fourth instar midge larvae). Important with SPME is the equilibrium approach. The device is supposed to be in a similar equilibrium with the surrounding sediment as a soil organism such as an earthworm. Van der Wal (2003) showed that SPME-fibres used in soil could predict bioaccumulation in oligochaetes. Using the SPME measured available fraction as indication for the water soluble part, the modelling of uptake in earthworms with the equilibrium partition theory also improved (Jager, 2003).

Moleculair extractions

Reid *et al.* (2000-a) used cyclodextrins, which are soluble in water due to a polar exterior and have a hydrophobic cavity in the interior. The principle is comparable with solid phase extraction, but instead of a solid material, individual molecules are used. The cavity in the cyclodextrin is easily accessible for PAHs. When present in the water phase, PAHs are encapsulated by the cyclodextrins (1:1 complex). Using extraction times of 20 hours, a good correlation with biodegradation has been obtained. After the extraction of the soil sample with cyclodextrins, the water phase is separated from the soil. The complexed PAHs can be extracted from the water phase with a non-polar solvent and analysed.

Solvent Based Extractions

Some approaches rely on the use of a single extractant. The approach is based on the assumption that the quantity of a chemical removed from soil by a mild or non-exhaustive extraction procedure will be similar to the amount that is bioavailable to one or more groups of organisms. Technically, mild extractions are comparable with methods used to measure the total concentration. The same instrumentation can be used as long as it is possible to decrease the extraction strength of the system (by decreasing extraction time, lowering temperature, or increasing water content to decrease the hydrophobic character of the solvent). Depending on the extraction strength or increasing rigor of the extraction procedure, the percentage extracted will differ. Examples are presented in Figure 3.8 in Section 3.5.

All extractions described in this section are empirical and chemical/physical understanding is limited. Changes in conditions will cause different results. Time is a logical variable, as described in 3.2, but there are more variables, such as the choice of solvent and pressure and temperature, as described below. Due to these variables, the method can be less robust than water based extraction. In general, the more variables, the less robust.

Mild extractability by several organic solvents has been correlated with the availability of phenanthrene and atrazine to earthworms and micro-organisms (Kelsey *et al.*, 1997). Extractability with tetrahydrofuran-water has been correlated with the bioavailability of several organic compounds to earthworms (Tang and Alexander, 1998). Extraction with 70% acetic acid has been used to predict the portion of PAHs in sediments that are biodegradable (Doddema *et al.*, 1998). Methanol-water mixtures at different temperatures have been used to establish K_{oc} values in aged soils (Krauss and Wilcke, 2001-a). Jonker and Smedes (2000) used different percentages of methanol and extrapolated the results to the free dissolved concentration in water.

Another approach to extraction methodologies involves the use of an extraction system with multiple adjustable parameters. For ease of optimization and sample handling, as well as providing these additional adjustable parameters, one might consider automated extraction equipment as well as alternative extraction fluids. Two possibilities, currently under development, may be of value. These are Supercritical Fluid Extraction and Accelerated Solvent Extraction (see also section 3.4.1). Extraction conditions can be easily adjusted, which can be used for optimisation (maximum recovery) for measurement of the total concentration, but also to reduce the extraction efficiency in order to extract a less strongly bound, easily accessible contaminant. The use of SFE is described for determining desorption kinetics (Weber and Young 1997), as well as relative availability to chemical extraction (Rochette and Koskinen, 1996). The influence of aging on extractability has also been demonstrated through the use of milder SFE conditions with PAHs, petroleum hydrocarbons, and pesticides (Camel *et al.*, 1995). Using SFE under mild conditions, extracted amounts have been correlated to the results of biodegradation measured in laboratory experiments (Loibner *et al.*, 2000) and in a field experiment (Hawthorne *et al.*, 2001). ASE methodology has not yet been applied to mimic a biological response.

Weston *et al.* (1998-a and b) used digestive fluid to estimate bioavailability. Mayer *et al.* (1996) showed that use of these fluids led to an increase in solubility, but this could not be related to the uptake by deposit-feeders. As shown for heavy metals, (Rood, 2000) the physiological status of the gastro-intestinal conditions will also be important for the uptake of organic contaminants.

Selective oxidation of organic matter

Organic contaminants are most strongly adsorbed to the organic matter in the soil. Different types of organic matter can be distinguished (Weber *et al.*, 1992 and Pignatello and Xing, 1996). As in polymers, organic matter can be distributed into two phases: an expanded phase and a condensed phase. The expanded phase is a rubber-like phase, also called an amorphous phase (Luthy *et al.*, 1997). The condensed phase is a glassy phase. The strong binding between organic matter molecules is responsible for a strong matrix (Pignatello, 1998). In this matrix adsorption occurs in internal micro-pores or voids of several nanometres. To reach or leave these pores, diffusion through the condensed organic matter is necessary, which makes it a very slow process, much slower than desorption from the expanded phase. The latter can be considered as being the bioavailable fraction. Cuypers (2001) showed experimentally that it is realistic to make this distinction. He introduced a soft persulphate oxidation method for selective oxidation of the expanded phase. This phase was oxidised during 3 hours with $K_2S_2O_8$ in a slurry at a temperature of 70°C. PAHs adsorbed to the expanded phase were oxidised together with the expanded phase. The concentration of PAHs left in the residue (condensed phase) was a good estimate for the residual concentration after a bioremediation treatment. This method is an example of measurement of sequestered concentration because the available PAHs have been removed by oxidation.

Thermal desorption

Recently a number of research groups started to explore the potential for thermal desorption to differentiate the relative availability of chemical contaminants from soil. The premise behind this technique is that sequestered material should require more time and/or energy to be removed from soil samples. Previous thermal desorption experiments (Werth and Reinhard, 1997; Uzigiris *et al.*, 1995) have shown that thermal desorption spectra give biphasic desorption patterns much like solution-based desorption profiles. The experiments were not appropriate to differentiate between relatively available and sequestered compounds in a single sample of soil.

A coupled thermal desorption mass spectrometer has been used to study desorption of aged hydrocarbons from soil. This coupled arrangement is only possible when the desorbed contaminants are ionized for introduction into the mass spectrometer in a gentle manner (e.g., photo ionization). Initial results suggest that the effect of ageing, clay content, and compound type is reflected in the shape and placement of the desorption curve (Zoller, Personal communication). Ghosh *et al.* (2001) used this instrumentation to measure the desorption rate from coal-derived particles.

Techniques Derived from Molecular Biology

An organism, or a system derived from an organism, that responds to a biologically available fraction of a toxicant may provide in the future the basis for an analytical technique for bioavailability. Such organisms may be engineered to contain a gene sequence that, in the presence of a toxin or substrate, will trigger the transcription of a reporter gene(s). The gene product may then be measured either directly (e.g., light from a *lux* cassette or fluorescent green protein), or indirectly through an enzyme assay (e.g., ß-galactosidase from a *lac* gene).

Bacteria that are responsive to the presence of aromatic hydrocarbons such as toluene and naphthalene (Appelgate *et al.*, 1998; Sousa *et al.*, 1998) and to certain genotoxic agents (Van der Lelie et a;., 1997; Alexander *et al.*, 1999) are being used. However, combining the organism, sensor function, reporter function, and assay system remains to be done efficiently In addition, this technique has to be validated to correspond to other receptors and environmental endpoints. The results from the approach must correspond to biological assays that are a surrogate for human exposure or that represents species or activities of ecological importance. Certain biosensor approaches are beginning to find their way to into use (Simpson *et al.*, 1998). Much work remains to be done before such systems can be designed, implemented, and correlated with human and ecological exposures. In aqueous solutions, biosensors can already replace the chemical analyses described above as a tool to determine biologically relevant fractions of contaminants. In actual soil matrices, however, biosensors are still subject to confounding factors.

3.5 Chemical methods used in this thesis to establish bioavailability

An important part of this thesis is the long-term experiment on Kreekraksluizen, which started in 1990. In the beginning, bioavailability was not a subject for research. Bioremediation was considered to be a technique that could remove all contaminants present in a limited amount of time. During the total duration of this investigation of bioremediation on landfarms, the concept of bioavailability has been developed worldwide. In 1991 the presence of a residual concentration in landfarmed soils was explained by limited bioavailability (Harmsen, 1991). It was, however, not yet possible to give a proper physical description of this limited bioavailability or to predict the residual concentration with methods described in this chapter. Limited diffusion (Wu and Gschwend, 1986) was already mentioned as an important factor, but there was still hope that the degradation rate could be increased. Later it was postulated that bioremediation of the residual concentration was only possible if a more time consuming method was used (Harmsen, 1993). Extensive (passive) landfarming, which makes use of the time factor, was introduced (Harmsen *et al.*, 1994) and an experiment to test this concept was begun. As part of the investigation on landfarming, research has been initiated to study the chemical measurement of bioavailability and the use of bio-assays to measure effects on organisms. During the same period, other scientists were also investigating bioavailability, and their results were adapted and applied to this study. Our experiments were first related to the possibility of biodegradation. As soon as reliable results could be obtained, the ideas on bioavailability were further developed in order to include also ecotoxicological risks (Harmsen and Ferdinandy, 1999). In the next paragraph, results of the research on chemical methods are summarised, illustrating the ideas and changes in ideas from 1995 onwards.

3.5.1 Availability of PAHs

At first, and in agreement with the radial diffusion model (Wu and Gschwend, 1986, Chapter 2), the bioavailable fraction was thought to be adsorbed on the surface of particles. Because the contaminants were on or close to the surface, they were able to diffuse in a short period to the pore water. There were two possible methods to extract the contaminants:

- Using a non or slightly water mixable solvent. With this procedure, the solvent would only reach the surface of particles and could not penetrate into small, water-filled soil pores.
- Using a water mixable solvent. In this procedure the sample would be extracted with this solvent mixed with water using a fixed concentration and a fixed extraction time. Using a short extraction period, this mixture could only extract the surface of soil aggregates.

Experiments were carried out with petroleum ether, hexanol and toluene (non water mixable) and acetone and acetic acid (water mixable). Results are presented in Doddema *et al.* (1998) and summarised in Figure 3.8.

Three sediments were investigated, using the chemical tests mentioned previously and with a biological test derived from Dechema (1992) to establish the degradable amount. The sediments originated from the Petroleum Harbour, which sediment also was investigated on the landfarm Kreekraksluizen (see other chapters), and from two other locations Overschie and Nieuwkoop. They showed degradabilities of PAHs in the biological test of respectively 68%, 9% and 34%. As expected, when using hexanol, petroleum ether and toluene, the amounts extracted increased with time. However, the results of the extraction did not correlate with the results of the biological test. Consequently these extractions were not been used further. Probably the interaction of these solvents with the surface of the sediments has nothing to do with processes occurring during biodegradation.

Extraction with both 50% acetone and 70% acetic acid did correlate with the biological test. (Figure 3.8 D and E). The slope of the acetone curve, however, was steeper, which makes the extraction with acetone less robust. With a steep slope, the method is sensitive to small changes in concentration of the solvent; therefore, the results of the acetone extraction will be more sensitive for small differences in water percentage in the extract. Therefore it was been concluded that the extraction with 70% acetic acid had more potential for further investigation.

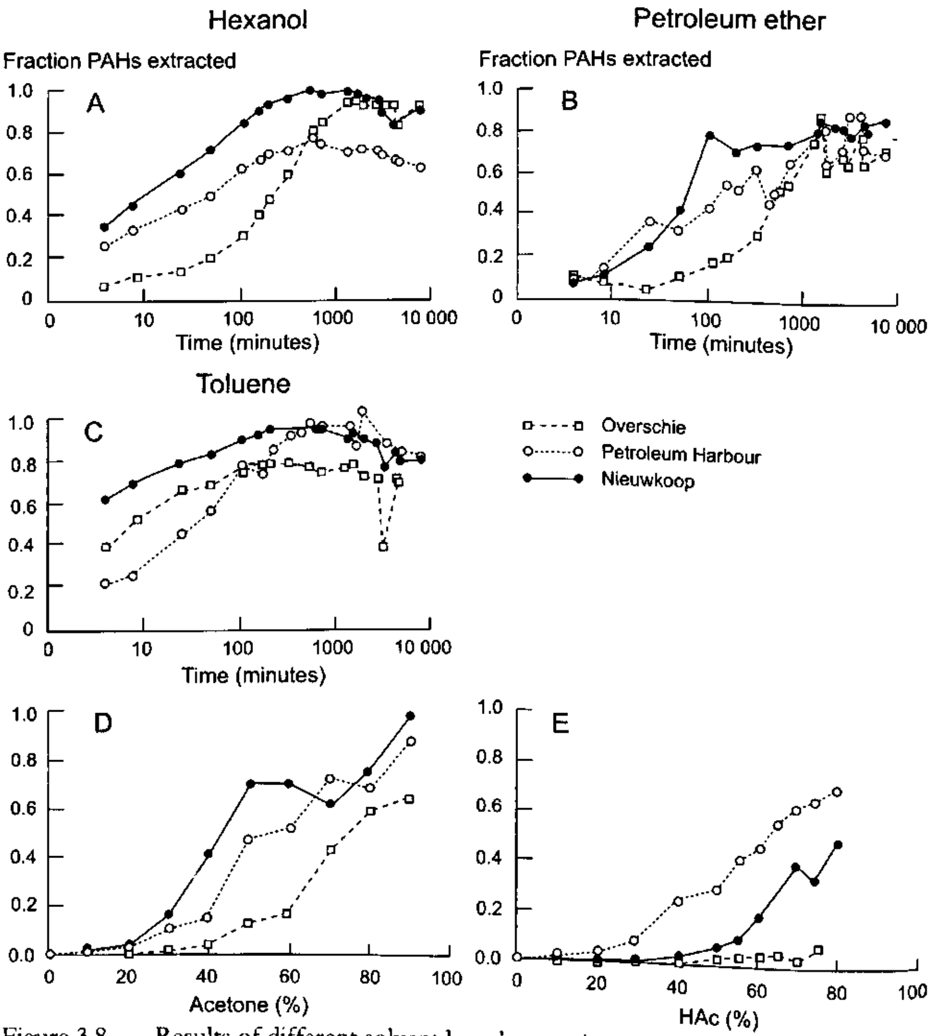

Figure 3.8 Results of different solvent based extraction procedures (Doddema *et al.*, 1998).

A Extraction with hexanol as function of time.
B Extraction with petroleum ether as function of time.
C Extraction with toluene as function of time.
D Extraction with different percentages of acetone in water.
E Extraction with different percentages of acetic acid in water.

In further testing the extraction of sediment with 70% acetic acid proved to give a good prediction for the biodegradability of light to heavily (class 3 and 4) polluted sediments (Figure 3.9). Using linear fitting through zero, R^2 values were respectively 0.88 and 0.96. The predictive power for low contaminated sediments (class 1 and 2; < 10 mg/kg) is smaller, probably due to inaccuracies in the measurements at this lower level of contamination (correlation coefficient $R^2 = 0.5$). Using 70% acetic acid, the extraction time has to be small (10 minutes) to assure that only the bioavailable fraction will be extracted. With an extraction time of 16 hours, this procedure was also able to extract the total amount present in the sediment. Because the extractant is able to enter the soil aggregates, this also indicates that mass transfer is the limiting step for bioavailability.

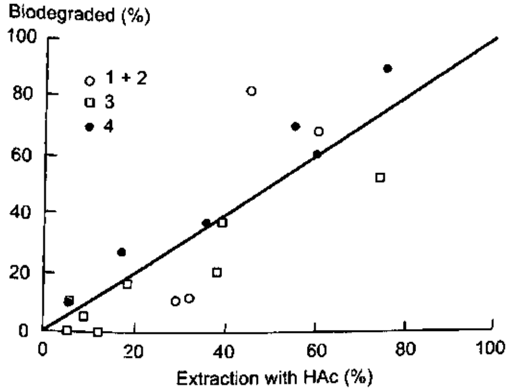

Figure 3.9 Biodegradation as function of the extracted PAHs (70% HAc) in different classes (1; 2; 3 and 4) of polluted sediments, in relation to the 1 to 1 line.

In the same period, Cornelissen *et al.* (1997) developed the Tenax-procedure. The method and results are described in more detail in Chapter 4 of this thesis. This method is based on a different principle than the solvent-based extraction method with acetic acid. It is a water-based extraction (see 3.4.3) and measures the amount desorbed via the water phase, which gives it a theoretical background. Both methods have been applied on sediments on Kreekraksluizen; results are given in Figure 3.10. Biodegradation is presented as the amount degraded in the first fast degrading phase of the Petroleum harbour sediment (see also Chapter 4). Both methods gave a good prediction of the biodegradation. The slope of the Tenax curve was closer to the 1 to 1 line than the acetic acid curve.

Other methods that could also be applicable give a good prediction of the degradable amount of PAHs, as reported in several publications. Methods using XAD (Northcott and Jones, 2001) and cyclodextrins (Reid *et al.*, 2000-a) are comparable with Tenax. Extraction with methanol (Krauss and Wilcke, 2001a) is comparable with 70% acetic acid. Also the persulphate oxidation of Cuypers (2001) gives a good prediction. These methods have, however, not been used, because they became available for use after the reported research had started, and it was not the intention of this study to compare several methods.

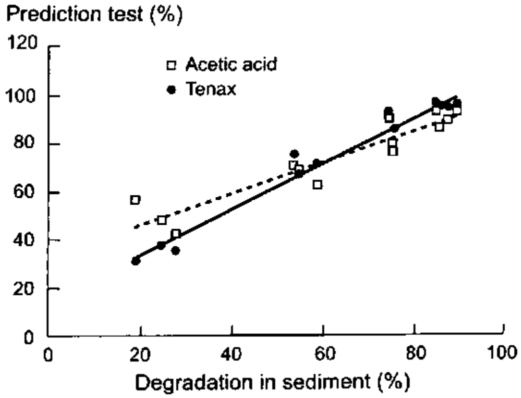

Figure 3.10 Prediction of biodegradation using chemical tests as a function of biodegradation of individual PAHs in fresh Petroleum harbour sediment. PAH, at the left in the figure are high molecular ones.

The results of the experiments with PAHs showed that methods having different mechanisms can give an estimate of the fraction available for fast degradation. Results of both water-based methods and aqueous-based solvents correlate well with the fast degradable fraction in different sediments. Reid *et al.* (2000-b) also came to this conclusion, because the methods are based on transfer to the aqueous phase. The water-based methods (e.g., Tenax) are measuring desorption, and extraction times of approximately 20 hours are necessary to be able to measure desorption and diffusion of the contaminant to pore water. In these 20 hours, stable levels of extraction are obtained, and a deviation of several hours has no influence on the results (robust method). With water mixable solvents (e.g., HAc) the solubility is increased. This increase creates higher desorption rates and enables measurement of desorption of the bioavailable fraction in a short period (e.g., 10 minutes), which can be an advantage if the method will be used in routine applications. An important disadvantage of solvent-based extractions is that small deviations in time, composition of the extractant, temperature, and added energy will influence the results. The procedure has to be exactly described and followed. Moreover, the mechanistic information obtained with a solvent-based extraction is limited, although Loibner (2003) suggest that the models describing rates in Supercritical Fluid Extraction are closely related to models used for the characterization of the sorption/desorption behaviour in real world samples. The Tenax method can also deliver kinetic parameters on desorption and as shown in Chapter 2, the slow desorption process to the water phase is important in the bioremediation process. The Tenax method measures this slow desorption and is a better method from a theoretical perspective. Therefore the Tenax method was chosen for further use in this research.

3.5.2 Availability of mineral oil

Although the polarity of mineral oil components is comparable with the polarity of PAHs, methods suitable for measurement of PÅHS are not suitable for mineral oil. Cuypers (2001) showed that the previously described persulphate method, which gives good results for PAHs, did not give a good prediction of the availability of mineral oil. An explanation is the higher resistance for oxidation of the aliphatic C-C bond in mineral oil molecules compared to the aromatic rings in PAHs. Also for Tenax, results are confusing. In two sediments with 50% degradation of mineral oil, using Tenax (20 hours desorption), we found in one sediment less than 8%, and in the other, 30% availability. Increasing the desorption time from 20 to 168 hours, Cuypers (2001) found a correlation with biodegradation, but we could not reproduce these results with the sediments we have investigated. Desorption is probably not the defining factor for biodegradation of mineral oil. It is also possible that analytical problems are responsible for the deviation. Tenax will also interact with mineral oil present as free phase and the free phase can preferentially adsorb desorbed oil molecules.

In experiments set up to obtain a better understanding of toxicity of mineral oil in sediment (Brils *et al.*, 2002), we did not found a relationship between the acetic acid extraction method and toxicity. We also did not find a relationship at other concentrations of acetic acid than 70% (Harmsen and Zweers, 2000). In this experiment, two types of mineral oil were spiked, diesel fuel (DMA) and lubricant oil (HV 46). Remarkable with these measurements was the effective extraction of mineral oil with pure water and low concentrations of acetic acid, which was not expected, because water is not a suitable solvent for the extraction of mineral oil (Figure 3.11). After microscopic investigation of the sediments, we came to the conclusion that weakly bound oil droplets had been extracted. This amount of weak adsorbed droplets correlated better with the results of bioassays (*Corrophium*) than the total concentration (Kater *et al.*, 2000). As shown in Figure 3.8, PAHs are not extracted at low acetic acid percentages.

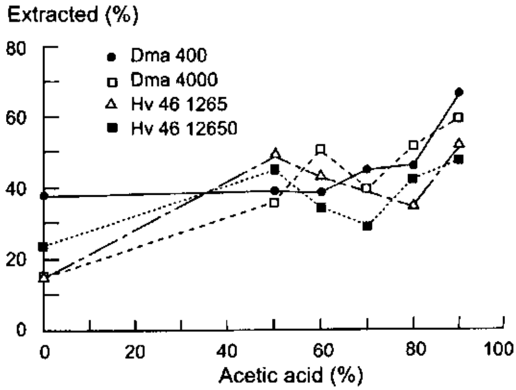

Figure 3.11 Extraction efficiency of mineral oil extracted with different water/acetic acid mixtures Samples used were spiked with a diesel fuel(DMA) and a lubricating oil (HV 46) at different added concentrations (in mg/kg d.m).

Partial extraction concentrations have to be compared with the concentration measured with a method designed to measure the total concentration. Remarkable in the experiments was the low recovery of added mineral oil using the agitation procedure to measure the total concentration described in NEN 5733. This was not only the case in this study, but has also been confirmed with sediments investigated by RIZA (RIZA, 2002). It was concluded that mineral oil was strongly adsorbed and not available for the acetone/petroleum ether mixture used in the method. Using a Soxhlet-procedure gave a higher recovery, but not in all samples. We also analysed aged sediments, where the agitation procedure gave higher concentrations. This variation in recovery using different methods has also been reported by Buddhadas (2002). Combining the different results, the following hypothetical distribution of mineral oil over different fractions in sediment is assumed:

- Free occurring, un-bound droplets.
- Droplets bound to sediment particles.
- Mineral oil adsorbed on the surface of organic matter.
- Mineral oil absorbed in the organic matter.
- Mineral oil present between mineral particles.

Different methods are suitable for analyses of the different mineral oil fractions as shown in Table 3.1.

Table 3.1 Mineral oil fractions in sediments and methods to measure or identify mineral oil (+ measured, - not measured).

Occurrence of mineral oil	Strength of binding	Method			
		Agitation with water or 50% HAc	Soxhlet	Agitaion Aceton/ Petroleum ether	Micro-scopic
Not bound oil droplets	Weak	+	+	+	+
Bounded oil droplets	Strong	-	+	+	+
Organic matter, adsorbed	Strong	-	+	+	-
Organic matter, absorbed	Very Strong	-	+	-	-
Between mineral particles	Very Strong	-	-	+	-

In addition to the physical classification presented in Table 3.1, other classifications are possible. Mineral oil is a mixture of many different organic compounds and has no constant composition. Gasoline and lubricating oil are both considered as mineral oil, but have completely different compositions. They have different boiling ranges, which can be used to classify mineral oil; in principle this is already done with gas chromatographic analysis (NEN5733 or ISO/DIS 16703). The chromatogram gives the composition of the analysed mineral oil arranged according to boiling points. By integrating part of the chromatogram, the concentration of a certain boiling fraction can be established. An important fraction is the fraction containing low boiling compounds (mineral oil compounds with less than 20 C-atoms). These compounds are in general more easily degradable and represent compounds toxic for organisms (Brils *et al.*, 2002).

Degradation of mineral oil does not follow the boiling point sequence. In degradability studies, the first compounds to be removed are the well recognisable n-alkanes, including even the high boiling ones (the n-alkanes in the chromatogram are visible as well-separated peaks). Branched alkanes and also low boiling branched alkanes are much more difficult to degrade. The molecular structure is therefore an important issue in degradation of mineral oil.

Another means of classification is the use of polarity, usually expressed as K_{ow}-values (distribution coefficient between octanol and water). Using these values it can be shown that the aromatic fraction in mineral oil will be the most toxic fraction (Verbruggen, 1999). Analytically it is possible to split the extracted mineral oil into a more polar, aromatic fraction and a less polar, aliphatic fraction. It will be clear that compounds in these fractions also have different boiling points.

From an analytical point of view, mineral oil is considered as non-polar. After extraction of a soil sample, the extract is cleaned up with Florisil (a prepared diatomaceous substance) to remove the co-extracted, more polar natural organic matter. This implies that all compounds that are polar enough to be adsorbed by florisil are not considered to be part of the mineral oil. Mineral oil products may contain partly oxidised components with toxic features. These components will not be measured, because they are adsorbed by florisil and excluded in the analysis.

These four ways of classification: physical, boiling point, degradability and polarity, make it difficult to develop a general applicable chemical method as a tool to measure the bioavailability of mineral oil. This is in contrast to contaminants that are present as separated molecules such as PAHs. On the other hand, the classification may also give an opportunity for development of an appropriate method. In other countries, research is going on for representative mineral oil fractions that have to be considered in the health risk assessment of mineral oil in soil (Environment Agency, 2003).

3.6 Discussion and conclusions

3.6.1 Implementation of bioavailability

Confounding factors

Several factors may confound chemical tests or may lead to the lack of correlation of an otherwise suitable chemical test with biological response. For example, in a soil containing mixtures of toxicants, there may be synergistic or antagonistic effects so that the influence of several toxicants may be greater or smaller than predicted from their effects when tested individually. Chemical procedures will not reveal these synergisms or antagonisms. Contaminants in soil sometimes exist in nonaqueous-phase liquids (NAPLs) or as crystalline materials (see also Figure 3.6), and the correlation between biological availability of compounds in NAPLs and crystals and the quantities detected by chemical procedures is presently unknown. The properties of some soils (e.g., pH values or structure) may result in an inhibition of the growth or activity of organisms independently of the presence or absence of toxicants, and the chemical tests will thus not be related to the relevant biological response. Furthermore, although the concentration-response curve for the chemical test may parallel the dose-response curve for a test organism (and thus represent a useful surrogate test) at low concentrations of a toxicant, the same may not be true at high concentrations (Figure 3.12).

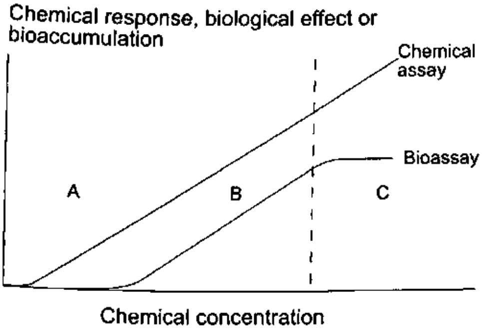

Figure 3.12 Comparison of a hypothetical response of chemical test and bioassays to an increasing concentration of a contaminant in soil. In region A, the contaminant is detected by chemical analysis, but there is no detectable biological effect. In region B, a parallel response is observed and correlation is possible. In region C, assays become non-linear and correlation is lost. Adapted from Alexander *et al.*, 2003.

Contaminants are often not homogeneously distributed in soil. Heterogeneous distribution can be represented by highly localised, small sites of contamination or large zones containing the toxic chemical. Organisms will be affected differently by the small sites or by the large zones of the contamination. In contrast, the chemical test will be based on analysis of a small sample of soil that (hopefully well-mixed) does not show locally high or low concentrations. Neither will it reflect the capacity of organisms to move away from zones of contamination (avoidance) nor the ability of organisms to integrate over time by accumulating different amounts, taken up at various sites with different contaminant levels.

Methods that reflect the actual plant-available concentration are useful to determine whether toxicity to the crop may occur or to predict the uptake by the plant. However, this requires mono-species vegetation with reasonable homogenized environmental conditions. Upon a change in either soil pH or organic matter as a result of management, phytotoxicity and extractable concentrations will change. Consequently heterogeneous natural vegetation with spatially different pH- and organic matter levels will show variable availabilities.

Calibration of phytotoxicity tests is complicated because roots can grow through surface soil, high in metal contaminants, and obtain nutrients and water from deeper soil horizons, which are less or non-contaminated. For this reason the response observed from pot studies is commonly much greater than measurements conducted in the field (de Vries and Tiller, 1978).

Koopmans (2004) showed that the predicted amount of available phosphorus (chemical test or model) and the uptake in the target grass species follow the curve in Figure 3.12. In P-saturated soils the available amount in the pore water is larger than the uptake by grass. The flux of phosphorus into the grass is the limiting factor and k_2

(constant described in 3.2.2) will be much smaller than 1. In this part of the curve, uptake was not limited by desorption. Growing grass for several years decreased the phosphorus content in the soil, and k_2 stabilised to a value close to one. Both the available phosphorus and uptake of phosphorus decreased. In this linear part of both curves, uptake was also limited by transport from the soil aggregate to the root, because the root system does not reach every soil aggregate (flux in the soil system is the limiting factor). The lowest part of the curve in which plant growth is inhibited by absence of phosphorus was not reached. Koopmans concluded that bioavailability should not be used as a static concept, but as a dynamic concept if it is used to optimise the situation for plant growth.

Scientific background and regulation

Chemical analysis of the bioavailability of contaminants in soil requires analytical testing in addition to the current methods that are used to determine total concentration. With the increased information gained through these tests, one can anticipate an increase in the total costs of soil analyses. Thus, it will be advantageous to implement appropriate protocols that minimise the extra costs and maximise the value of the extra-obtained information. This can be done through a tiered decision-making approach whereby redundant testing can be avoided and by the selection of an appropriate test organism(s) for which the chemical test is to be correlated early in the decision-making process.

An example of a tiered approach is a soil or sediment sample with significant levels of a contaminant that readily desorbs from the soil into an aqueous medium. Contaminants are then readily available for biological uptake, biodegradation and transport, and it will not be necessary to perform an extensive evaluation of bioavailability potential. Conversely, if a soil contains contaminants that are resistant to desorption, information from chemical analysis has no value for prediction of environmental effects. Current testing of total concentrations of soil contaminants could be augmented by a method suitable to measure the availability of a specific contaminant as a basis for initial decision making, or it may modify the current regulatory paradigm.

The percentages of the total available concentration of a compound will vary with different uptake mechanisms and different species. This could lead to the assumption that different chemical tests must be correlated with a wide range of dissimilar species. Such an approach would be expensive, time consuming, confusing, and difficult to integrate into a regulatory system. Two alternatives can be considered. First, a conservative approach can be used in which the test organism is able to acquire the highest percentage of the total concentration of the toxicant in soil (i.e., more than any other species). This would offer the highest degree of protection to ecological receptors, but it also may be overprotective of the natural functioning of ecosystems. A second approach would rely on the use of a test organism (for correlating bio-assay and chemical tests) that is most relevant for, or has special importance for, the particular land use associated with the contaminated soil.

Neither of these approaches needs to be considered when humans are the species of concern for exposure at the site. In this case, the result of the chemical test needs to be correlated with some measure of bioavailability to humans by the dermal, ingestion, or inhalation routes of exposure.

Chemical tests offer considerable promise for providing meaningful information that will be useful in developing realistic information for risk analysis of contaminated soils and sediments and for decision making in regard to polluted sites. Additional research and development are clearly necessary. It should be realised that there is no such thing as the ultimate test for the measurement of bioavailability. Depending on the question of acute or chronic toxicological effects, degradation, leaching, and health of human beings, different tests will be necessary. To avoid this use of multiple tests, a process of harmonisation followed by standardisation is needed.

This harmonisation/standardisation process should be developed in cooperation with regulators and combined with education of the public. Regulators and the public are familiar with a system in which total concentrations are related to the necessity for clean up, target values for remediation, and values for reuse of contaminated soil. The measured total concentrations are considered as well founded and as definitive values. People responsible for polluted locations observe that in these locations the first phases of natural development occur (succession of vegetation) and are often not hampered by presence of contaminants. They understand that this may be caused by a low bioavailability of the contaminant. Results of bioassays, used as a tool to manage these sites, are however still considered as ‘soft’ data. If more than 75% of test organisms die, there is a problem, but is the problem solved if only 5% (HC_5-value) should die? Thinking on a human scale, this is not acceptable. Regulators, however, are responsible for the decisions and not scientists, who have produced the data on risks. As long as data on bioavailability do not have a strong scientific base and when there is no experience with application of these data, regulators will return again to use of the ‘definitive’ total concentrations (Figure 3.13).

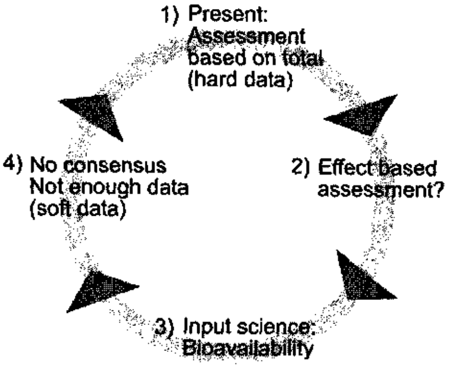

Figure 3.13 Decision making on hard and soft data.

It will be very important to present the concept of bioavailability including the possibilities of measurement in such a way that it is considered as definitive. It is possible to change the 'reference framework' for regulators as can be learned from the introduction of the Building Act in the Netherlands. The values for multifunctionality that were in use hampered the reuse of cleaned soils. After introduction of a system in which a higher total concentration had to be combined with a leaching test, the reuse of cleaned soils increased tremendously. By defining the limited use as for building material, ecological risks were not of interest anymore. Risks were only related to leaching, which can be estimated with accepted test procedures.

During the development of methods for bioavailability, the use of complex and expensive methods is acceptable, because in this period, the scientific foundation of the methods is important. Several variations on the same principle provide even more confidence. For regulations, comparability and costs are more important. Regulations require simpler, preferably standardised methods. It will be complicated to reduce the large number of methods investigated to a limited number of methods for national and international regulating proposes. Each laboratory and each country will claim to have the best method. The latter can only be prevented when scientists do not start a methodological discussion but give minimum requirements for the methods necessary to establish bioavailability. Such a discussion has already started in ISO/TC190, Soil Quality. In this discussion it is necessary that scientists with knowledge on the behaviour of contaminants in soil, biologists, and ecologists work together to prevent different explanations of bioavailability. Without an interdisciplinary approach, bioavailability will remain an interesting scientific tool but will not play its necessary role in a sustainable approach to treatment of contaminated soils in the 'real' world. In 2003 a working group of ISO/TC190 was formed to develop guidelines for the use of bioavailability in soil and site assessment.

3.6.2 Bioavailability; definition and tools used in this thesis

In this chapter it has been shown that bioavailability is not a unique, fixed concept with a single meaning for all users. Depending on the background of the user, different definitions exist. This is not a problem as long as bioavailability is used in connection with a biological process or effect. If this connection is not made, it will stay a confusing concept. In this thesis bioavailability is further used in combination with biodegradation of PAHs and mineral oil. As presented already in 3.6.2, bioavailable for degrading organisms is defined as:

> *The amount of PAHs and mineral oil that can be transported (by diffusion or physical change of the adsorption site) to a site with a degrading micro-organism in a defined time period and that can enter the bio-influenced zone of this organism.*

This is a conceptual definition that can be used for all bioremediation techniques. Time may vary from days to weeks in a bioreactor and from years to decades in a more natural remediation system. In an infinite time period, the bioavailable fraction will theoretically equal the total amount of contaminants. Therefore an operational definition of bioavailability is necessary, which has been used in this research. As an operational definition, the bioavailable fraction is defined as:

> *The amount that is degraded aerobically on a landfarm in one year, under Dutch climate conditions*

Chemical methods can be used as a tool to predict biodegradation. Results of chemical methods cannot be defined as the bioavailable fraction but can only be used as an estimate of the bioavailable fraction. Several methods are available, described and also used in this investigation. For the availability of PAHs, the Tenax-method gave good predictions of biodegradation. We have chosen the Tenax-method for the following reasons:

- The mechanism used in the Tenax-method is diffusion. Diffusion is also used in the description of the rate of degradation (see Chapter 2).
- It is possible to derive kinetic parameters from the measured results.
- The Tenax-method was already available in 1997, when we started the availability measurements on Kreekraksluizen. To be able to compare results we used the method also in following years.

Methods developed later and using other principles such as the oxidation method of Cuypers (2001) could also be used and in that case organic matter fractions with different stabilities can explain the bioavailability mechanism (see Chapter 2). The choice of Tenax does not mean that it is the most suitable method for routine applications. That was not a part of our research. The method used supplied the necessary scientific data to get a better understanding of slow biodegradation. Which method or methods should be used as a standard method should be discussed in the ISO TC190 working group.

There is no chemical tool yet available to predict the bioavailability of mineral oil. Mineral oil is a complex mixture of components with different characteristics and is present in different phases. Mineral oil is strongly associated with the organic matter in sediments. A relationship has been found between the presence of small droplets and toxicity.

In this chapter the concept of bioavailability has been explained and defined in relation to biodegradation. It is possible to use chemical tools to predict the bioavailable (=biodegradable) fraction of PAH. These tools are used in the following chapter, for explanation of the slow degradation rates found in landfarming of contaminated sediments. It will also be discussed if the chemical tool can be correlated.

4 Degradation and desorption of PAHs in sediments: kinetic approach

4.1 Introduction

PAHs in soil and sediments are biodegradable as explained in the previous chapters. Successful bioremediations of sediments in pilot scale bioreactors have been reported (Ferdinandy, 1999; Jee *et al.*, 1998, Giordano *et al.*, 2003) and on landfarms (see Chapter 1). Degradation of PAHs in landfarms is an aerobic process and starts as soon as oxygen is present in soil pores. Because sediments are fully saturated with water, they are anaerobic. Dewatering, a process whereby water filled pores are replaced by air filled pores, is necessary. As soon as the oxygen concentration is high enough for biodegradation of the contaminant, a degradation pattern will be achieved as presented in Figure 4.1. Bioremediation in landfarms, and in other bioremediation systems, show the same pattern. The time necessary for biodegradation on a landfarm is much larger than the adaptation period for micro-organisms (see also Chapter 2.3) and generally no delay in degradation is observed. If dewatering of the sediment is the limiting step, then a delay period will be observed. The following observations are important:

- The degradation pattern exhibited a fast phase followed by a slow phase.
- The residual concentration at the end of treatment may vary in different sediments.

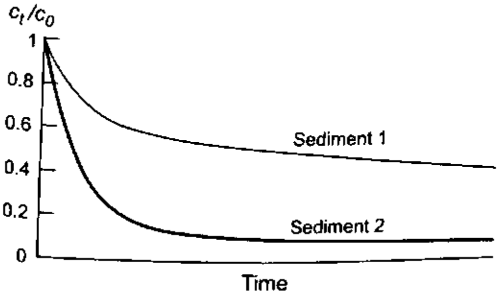

Figure 4.1 Characteristic pattern of bioremediation of sediment. Relative concentration c_t/c_0 as function of time. Time necessary for dewatering is ignored.

Uncertainty in the achievable residual concentration and the time needed to attain this concentration, will constitute a stumbling block to further practical development of landfarming of polluted sediments, especially when it necessary to attain a specific target value. Therefore, it is necessary to know which value can be attained and how much time is necessary to attain this value. To be able to predict the results of a bioremediation effort, it is necessary to know which processes are responsible for the existence of the different phases.

Which micro-organisms are responsible for the degradation of the different PAHs, has not been established. In a landfarm typically a large population of micro-organisms are present varying from small bacteria to large fungi. As presented in Chapter 6, fungi have good capabilities for the degradation of chemicals with multiple ring systems.

As long as the presence of oxygen is the limiting factor, the degradation rate can be explained by the rate of aeration as described in the previous Chapter 2. As soon as the landfarm is fully aerated (see also Chapter 6), and the available part of the PAHs has been degraded, different theories that were described in Chapter 2 may be used. These theories share a common concept that the contaminant is present on a site without active micro-organisms. This means that either the contaminant has to diffuse to another site containing a micro-organism, or that the site has to change in such a way that the availability for colonization by degrading micro-organisms increases. The following rate setting processes are considered:

- **Diffusion.** In the first soil models describing slow desorption, soil has been proposed as a porous sphere (Wu and Gschwend, 1986). In the case of bioremediation, the contaminant diffuses through the soil sphere from the inside (high concentration) to the surface (outside) where it is degraded (concentration is zero). This approach is further worked out in Chapter 2. Important in diffusion models are the molecular diffusion constant, the distribution constant (the stronger the adsorption to the solid phase, the slower the diffusion) and factors describing the complexity of the soil matrix. Using this theory, the rate constant has a physical meaning and factors responsible for the degradation rate can be recognised.
- **Stability of the (organic) soil matrix.** The different degradation rates can be given a physical background by introducing the ideas of different types of organic matter. (Weber *et al.*, 1992 and Pignatello and Xing, 1996). In this approach diffusion in the organic matter is still the rate-defining step. Like in polymers, organic matter can be distributed into two phases: (1) an expanded phase, and (2) a condensed phase. The expanded phase is a rubber like phase, also called amorphous phase (Luthy *et al.*, 1997). Sorption is linear, the diffusion constant does not depend on the concentration and there is no hysteresis. The condensed phase is a glassy phase, where sorption is non linear, the diffusion constant depends on concentration and hysteresis occurs. The strong bindings between organic matter molecules are responsible for a strong matrix (Pignatello, 1998). Within this matrix adsorption occurs in internal micro-pores or voids of several nanometres. In order to reach or leave these pores diffusion through the

condensed organic matter is necessary, which makes it a very slow process that is much slower then desorption from the expanded phase. Another way to affect desorption is to change the properties of the condensed phase. This phase is stable, but not inert. Thermal treatment (Bonten, 2001) changes condensed into expanded organic matter, but such a process is less applicable in landfarm and other natural systems. In the long term, however, organic matter is subject to change (degradation). Without addition or formation of new organic matter, all organic matter will degrade and oxidise in the long term. The changes in organic matter may happen within treatment times as described in this chapter (see also Chapter 2.2.3).

In both cases it is possible to use the multi-compartment model as a mathematical description of decrease of the contaminant concentration. Assuming that no interaction takes place between the compartments considered, the model can be described as a sum of first order decreases. Based on the results of the presented experiments in this chapter three compartments can be distinguished. The amount of PAHs present in the three compartments differs with the sediment. If the fraction of PAHs present in one of the compartments is zero or ignorable a two compartment model remains. Every fraction is described with two constants, the size and the rate constant k as follows (4.1):

$$\frac{c_t}{c_0} = F_{fast} \cdot e^{-k_{fast} \cdot t} + F_{slow} \cdot e^{-k_{slow} \cdot t} + F_{very\,slow} \cdot e^{-k_{very\,slow} \cdot t} \qquad (4.1)$$

where:

c_t = sediment/soil sorbed amount (mg/kg d.m.) at time t
c_0 = sediment/soil sorbed amount (mg/kg d.m.) at time 0
F_{fast} = fast desorbing/degrading fraction
F_{slow} = slow desorbing/degrading fraction
$F_{very\,slow}$ = very slow desorbing/degrading fraction
k_{fast} = rate constant fast desorption/degradation (y^{-1})
k_{slow} = rate constant slow desorption/degradation (y^{-1})
$k_{very\,slow}$ = rate constant very slow desorption/degradation (y^{-1})
t = time (y)

The sum of the fractions equals 1, which implies that the model contains 5 parameters which values have to be established. As shown in Chapter 2, it is possible to describe the rate constants with physical constants and properties of the soil (ripened sediment). Important parameters are the moisture content and the radius of soil aggregates.

The goal of this chapter is to deliver an effective tool for the prediction of results of landfarming of PAHs-contaminated sediments, using theories on diffusion and decomposition of organic matter in Chapter 2 and the concept of bioavailability described in Chapter 3. The experimental results in this chapter are based on a long-term experiment on the landfarm Kreekraksluizen. The first experiments were initiated in 1990. Sediments have been treated with intensive landfarming followed by passive landfarming. Due to the long treatment times it was possible to establish degradation rates during the different phases of treatment. During this treatment the concept of bioavailability was further developed. In the second half of the nineties it became possible to measure the fast desorbable fraction of PAHs as an estimate of the fast degrading fraction in the sediment, including the kinetics of the desorption process.

4.2 Materials and methods

4.2.1 Degradation experiments (field)

On an experimental field at Kreekraksluizen, situated in the province of Zeeland in the Netherlands, landfarms were initiated on semi-field scale. The first experiments were initiated in 1990 on fields equipped with a drainage layer of 30 cm. The fields were 20 * 7 m, about 50 cm of dredged sediment was applied and the layer thickness of the dewatered sediments was also about 30 cm. The sediments were intensive treated to stimulate biodegradation during the first years. The sediments originated from the Geul Harbour (GH) in Rotterdam and the harbour of Zierikzee (ZZ). Treatments used were: cultivation, no cultivation, adding of wood chips and adding of PAHs-adapted sludge from a sewage system. For all treatments used biodegradation occurred, but there were no significant differences between any of the several treatments (De Groot and van Lierop, 1995). Between the years 1990 and 1993, the PAHs-concentration (Dutch National List) in GH and ZZ were reduced, respectively, from 52 to 3.7 and from 65 to 18 mg/kg d.m. In 1993 the sediment from the different experimental fields were combined into two new experimental fields containing the Geul Harbour and Zierikzee sediments in a thicker layer. These sediments were further treated in a passive way (passive landfarming) and results are presented in this chapter.

In June 1994, the landfarm was extended with four fields for the treatment of sediment from the Petroleum Harbour (PH) in Amsterdam and sediment from the harbour in Wemeldinge (WEM), also situated in the province of Zeeland. In these fields an original layer thickness of about 1-meter has been used. In one field of each sediment dewatering has been stimulated with vegetation (passive landfarming). Both second fields were intensively cultivated in the first period of intensive landfarming of two years to stimulate dewatering and degradation (Figure 4.2). Dewatering is further discussed in Chapter 6. Original (fresh) PH and WEM sediments have been stored under wet anaerobic conditions in 200 l vessels for further studies like the desorption studies described in this chapter.

Because of the high PAHs-concentration in Petroleum Harbour sediment, this had to be considered as chemical waste. We were unaware of this at the start of the experiment and special permissions were necessary. Activities on the landfarm could only be initiated after receiving all permissions (November, 1994). Cultivation initiated in the following winter, which means that the first summer was not an effective period for bioremediation.

The inhomogeneity of polluted soil or sediment is very important in a field experiment. To be able to construct reliable degradation curves all fields were sampled very intensively. In order to achieve the desired accuracy at least 5 samples were taken per date, field and layer. At the initiation of the landfarms additional samples were necessary to achieve the desired confidence.

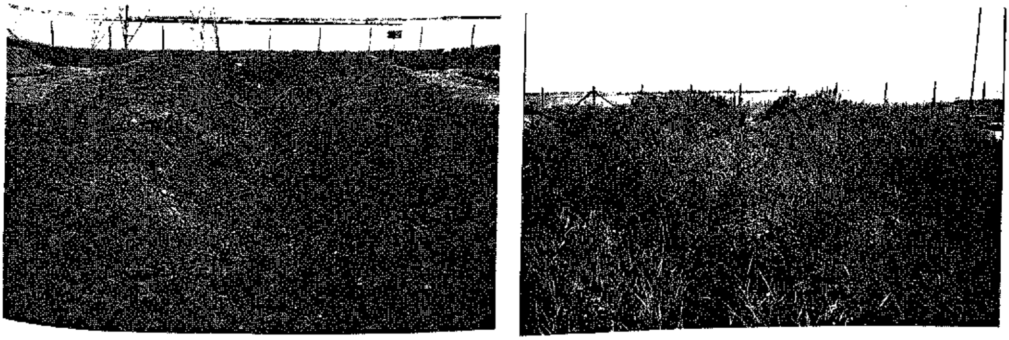

Figure 4.2 The Petroleum Harbour landfarms on Kreekraksluizen. Left the cultivated landfarm in 1995. Right the vegetated landfarm in 1997.

In the vegetated landfarm the upper layer was dewatered and ripened much faster than the lower layer and they were therefore sampled separately. The lower layer was defined as the (partly) anaerobic layer of the sediment. Due to increasing of the ripening this layer became thinner in following years. The different treatments are summarised in Table 4.1.

Table 4.1 Sediments investigated on Kreekraksluizen.

Type of sediment	Intensive landfarming (period)	Passive landfarming since	Number of layers sampled	Vegetation present since	PAH-NL concentration in original sediment (mg/kg d.m.)
PH, cultivated	1994 - 1996	1996	1	1996	550
PH, vegetated		1994	2	1995	550
WEM, cultivated	1994 -1996	1996	1	1996	45
WEM, vegetated		1994	2	1995	45
GH	1990 – 1993[1)]	1993	1	1993	52
ZZ	1990 – 1993[1)]	1993	1	1993	65

[1)] De Groot and van Lierop, 1995

Samples were analysed for PAHs using HPLC and fluorescence detection, according the Dutch standard method NEN 5771 (equivalent to ISO 13877). The wet sediments were extracted with a mixture of acetone/petroleum ether. The acetone was removed by extraction with water. The petroleum ether extract was concentrated using Kuderna Danish equipment to a volume of 10 ml. One ml acetonitril was added the 10 ml of petroleum ether and the solution was concentrated to a volume of one ml using nitrogen. A volume of 20 µl of the remaining acetonitril solution was injected on the HPLC-system. After on-line clean up with a 1 cm C8- column (Prospect, Spark Emmen) the PAHs were separated on a Vydac 201TPS4 RP C18 column of 20 cm and detected on a programmable fluorescence detector, programmed according NEN 5771. Peaks were measured as peak highs against an external standard. The PAHs as presented in Table 4.2 were measured. The most volatile PAHs are not reported because they are normally only present at low concentrations in sediments, they are biodegradable and it was not possible to accurately measure the residual concentration after the first fast degradation. Especially the naphthalene measurement was inaccurate and these poor results would influence the sum of PAHs too much. In the table is also listed those PAHs that are part of the Dutch National List. Because naphthalene is not reported, presentation of values of the Dutch National List means without naphthalene. Dibenzo[a,h]anthracene has been measured, but data were very unreliable due to the presence of a disturbing peak in the chromatogram and also was not reported. All results are expressed as concentration in the dry matter of the sediment (mg/kg d.m.).

Loss of mass on ignition was used as a simple method to estimate the organic matter content. Although it is known that this method may give systematic errors by analysing sediments (Frintrop, 2000), the results can be used to give a good impression of the stability of or the relative decrease of the organic matter.

Table 4.2 PAHs measured in sediments from the landfarm Kreekraksluizen.

PAH	Abreviation used		Number of aromatic rings	Dutch National List
Naphthalene		Not reported	2	X
Acenaphthylene		Not reported	2	
Acenaphthene		Not reported	2	
Fluorene	FLU		2	
Phenanthrene	PHE		3	X
Anthracene	ANT		3	X
Fluoranthene	FLT		3	X
Pyrene	PYR		4	
Benz[a]anthracene	BaA		4	X
Chrysene	CHR		4	X
Benz[b]fluoranthene	BbF		4	
Benz[k]fluoranthene	BkF		4	X
Benz[a]pyrene	BaP		5	X
Dibenzo[a,h]anthracene		Not reported	5	
Benzo[g,h,i]perylene	BPE		6	X
Indeno[1,2,3-c,d]pyrene	IPY		6	X

4.2.2 Desorption experiments (laboratorium)

From 1997, samples were also investigated using the Tenax desorption technique described by Cornelissen *et al.* (1997) to establish the bioavailable fractions and the kinetic of desorption. This technique was also applied on samples of original Petroleum Harbour and Wemeldinge sediment, which were stored in 200 l vessels under anaerobic conditions. In the applied procedure, the sediment (1g), water (50 ml), $HgCl_2$ (1.25 g/l) to stop the activity of degrading organisms and Tenax beads as adsorption medium (0.2 g) were brought into a separation funnel. The funnel was continuously shaken at room temperature (approx.20 °C), at such a rate that the sediment and Tenax beads were dispersed. Tenax TA (177-250 µm), a porous polymer based on 2,6-diphenyl-*p*-phenylene oxide was obtained from Chrompack. Before use the Tenax beads were rinsed with hexane, acetone and water (25 ml/g Tenax for all three solvents) and dried overnight at 75 °C. At selected times the Tenax was separated from the sediment suspension and analysed; fresh Tenax was added to the sediment suspension. Separation of Tenax from the sediment was possible, because the sediment sank to the bottom whereas the Tenax beads floats on the top and adhered to the glass wall of the separation funnel during separation. The Tenax residues were extracted with hexane and further analysed according the method for sediments. From the results the size of the fast desorbing fraction and the rate constants for the fast and slow desorbing fraction were calculated by a fitting procedure (Excel solver). In 1999 and 2001 samples were investigated using the one step procedure described by Cornelissen *et al.* (2001). During 6 hours 2 g of sediment was shaken with 1.5 g of Tenax. PAHs in Tenax and left in the sediment were measured according to the already prescribed methods.

4.2.3 Calculation of rate constants

As presented in Chapter 2, processes responsible for degradation can be fit with exponential curves (first order decrease) and theoretically the degradation curve can be fitted with a sum of different first order decreases (multi-compartment model). The preconditions to use the multi-compartment model cannot be fulfilled during landfarming of sediments. For the fast degradable fraction the kinetics of degradation are set by the rate of dewatering and not by diffusion and microbiological activity. A fit with a multi-compartment model would underestimate the degradation rate constant for fast degradation, but this underestimation would also lead to an underestimation of the slow degradation rate constant. Moreover no experiment was available showing all three compartments. Even if all compartments are included in the experiment, use of the two compartment model (3 parameters) is recommended over the three compartment model (5 parameters) (Johnson *et al*, 2001). Using a two compartment model, the value for the rate constant of the slowest process will have the lowest reliability (Opdyke *et al.*, 1999). Therefore, degradation curves have been fit with single exponential curves (Excel). To do this, linear parts of the degradation curve (plotted as the logarithm of the contaminant concentration versus time) were selected and fit. The obtained degradation rate constants have to be considered as actual constants. They are representative for the actual slope of the degradation curve.

Comparable with other researchers using Tenax, desorption data have been fit with a two-compartment model (fast and slow desorption) using the Excel-solver. For Tenax this is correct, because no re-adsorption occurs during the Tenax-desorption experiment. This means that the rate constant for fast desorption is not the actual one, but that the size of the fast fraction has been taken into account in the calculation. The rate constant for slow desorption has to be considered as actual, because the very slow fraction is not taken into account. The very slow desorbing fraction was not recognisable within the time frame of the desorption experiments. The actual slow desorption rate constant can be compared with the actual slow degradation rate constant.

4.3 Results

4.3.1 Degradation of PAHs

Homogeneity of the fields

In laboratory degradation studies it is possible to start with well mixed homogeneous sediment. As a result of mixing, standard deviations will be small and clear degradation curves can be obtained. On the scale of the experiments on Kreekraksluizen mixing is not possible and higher standard deviations have to be expected. In order to construct reliable degradation curves intensive sampling is necessary.

Because treatment of he Petroleum Harbour and Wemeldinge sediment in the first half year was not allowed, dewatering was very poor (see also Chapter 6) and degradation could not start because of the remaining anaerobic conditions in most of the sediment present on the fields. Degradation really started in next spring (1995). All the PAH-values measured in samples taken from anaerobic sediment in the first half year, have been used to make distribution curves of the PAHs-content in both sediments (Figure 4.3). As expected large differences in concentration have been measured, but no 'hot spots' could be recognised in the landfarm.

In both sediments the absolute levels differ by a factor of 10. Petroleum Harbour sediment is representative for a heavily polluted site, not only polluted with PAHs, but also with mineral oil (13,500 mg/kg d.m.). Wemeldinge sediment is representative for a lot of Harbours in the Netherlands (mineral oil 2,000 mg/kg d.m.).

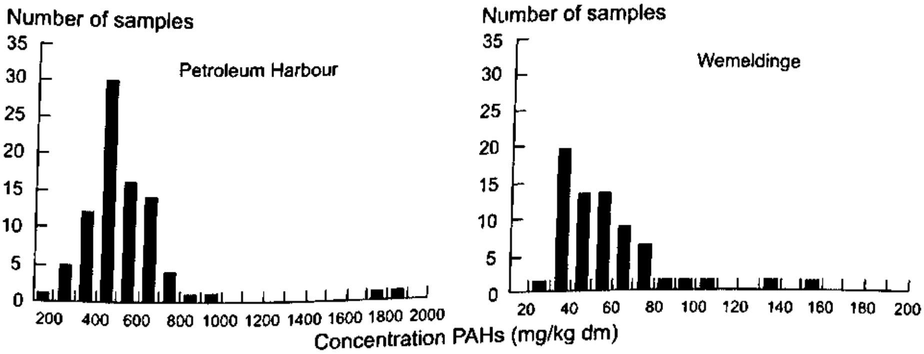

Figure 4.3 Distribution curve of the PAHs-content (sum Dutch National List) in Petroleum Harbour and Wemeldinge sediment representative for the start of the landfarm (1994).

Degradation rate of PAHs in Petroleum Harbour fields

In the upper layer of the vegetated landfarm, aerobic conditions were already developed during the first summer. Therefore the fastest initial degradation occurs in this layer. The degradation curves can be fit with two exponential curves (Figure 4.4). In this figure degradation curves are presented of the PAHs of the Dutch National List and of four individual PAHs. Similar results were obtained with the other measured PAHs. After 1 year, aeration was not the limiting factor in the upper layer and fast degradation was followed by slow degradation.

In the cultivated field more time was necessary to obtain aerobic conditions. By cultivation the aerated upper layer was mixed again with anaerobic sediment from the lower layers and two years were necessary to obtain a field aerated over the whole depth. This is visible in the degradation curve. Fast degradation took also 2 years, followed by slow degradation in the next years. In the cultivated as well as in the upper layer of the vegetated landfarm the first fast degradation period corresponds with the period to obtain a fully aerated sediment.

If it had been possible to start cultivation immediately, a higher fast degradation rate might have been obtained in the cultivated landfarm. The obtained degradation rate constants are the constants that belong to an aerobic landfarm as applied on Kreekraksluizen. Figure 4.4 also shows the large spreading in measured PAH-concentration as discussed in the previous sub-chapter and the necessity to analyse large number of samples. Values of the degradation rate constants for the sum of PAHs and individual PAHs, derived from an exponential fit of the log-linear parts of the curves, are given in Table 4.3.

Because of the poor aerobic conditions in the lower layer of the vegetated landfarm the initial degradation rate is smaller and the first fast degradation cannot be recognised, which is illustrated for fluorene in Figure 4.5. The degradation rate in the first years is much lower compared to the rate in the upper layer. In spite of the low initial degradation rate in the lower layer the same residual concentration is obtained after 7 years. This was also the case for the other individual PAHs. The data from the lower layer are fitted with one exponential curve, giving an average rate constant for fast and slow degradation (k_{f+s}).

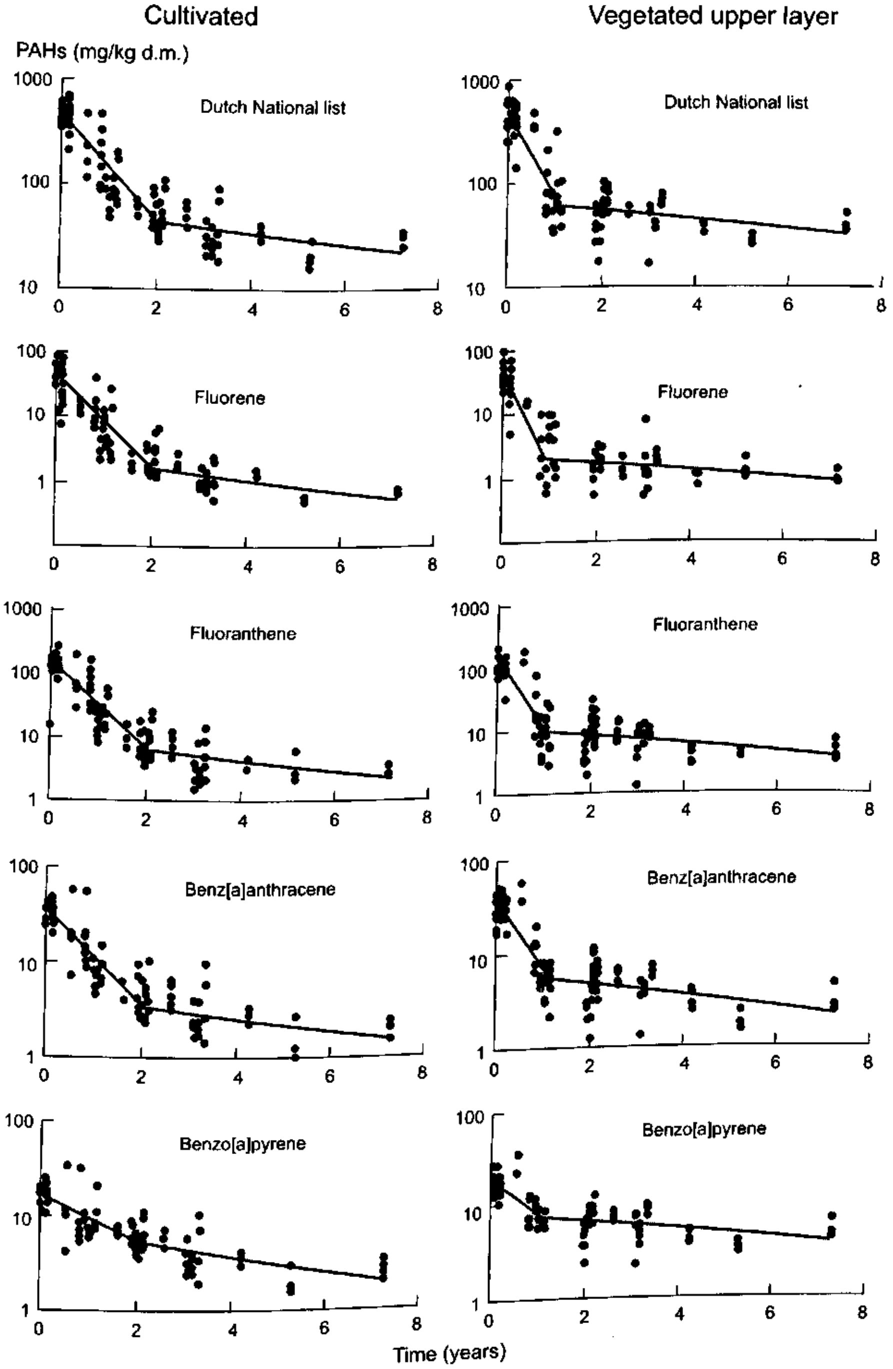

Figure 4.4 Degradation of PAHs in the Petroleum Harbour sediment. Left cultivated landfarm and right the upper layer in the vegetated landfarm.

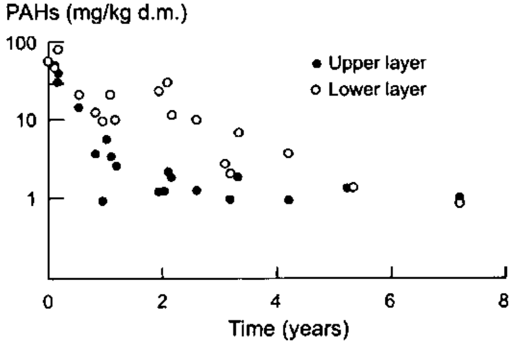

Figure 4.5 Degradation of fluorene in the vegetated Petroleum Harbour landfarm, upper layer and lower layer. Presented data are the average concentration per sampling date.

Table 4.3 Degradation rate constants of PAHs (y^{-1}) in the investigated sediments. (A) = actual value.

PAHs	PH					WEM			GH		ZZ
	Cultivated		Vegetated upper layer		Vegetated lower layer	Cultivated	Vegetated upper layer	Vegetated lower layer	Passive landfarm		Passive landfarm
	k_{fast} (A)	k_{slow} (A)	k_{fast} (A)	k_{slow} (A)	k_{f+s} (A)	k_{slow} (A)	k_{slow} (A)	k_{f+s} (A)	k_{slow} (A)	$k_{very\ slow}$	k_{s+vs} (A)
Dutch National list	1,19	0.13	2.04	0.10	0.38	0.068	0.037	0.12	0.15	0.041	0.016
Fluorene	1.61	0.20	3.99	0.13	0.57	0.17	0.14	0.26	0.15	0.097	
Phenanthrene	1.69	0.12	3.68.	0.04	0.54	0.11	0.055	0.17	0.08	0.048	
Anthracene	1.55	0.13	3.37	0.16	0.52	0.070	0.077	0.17	0.23	0.044	
Fluoranthene	1.47	0.19	2.48	0.15	0.50	0.078	0.019	0.087	0.26	0.071	
Pyrene	1.46	0.17	2.13	0.15	0.47	0.062	0.030	0.084	0.09	-	
Benz[a]anthracene	1.12	0.15	1.55	0.14	0.36	0.071	0.029	0.088	0.15	0.072	
Chrysene	0.87	0.17	1.22	0.13	0.28	0.054	0	0.017	0.25	0.044	
Benz[b]fluoranthene	0.70	0.16	0.73	0.12	0.20	0.055	0.028	0.063	0.18	0.041	
Benz[k]fluoranthene	0.78	0.15	0.89	0.13	0.22	0.054	0.029	0.056	0.12	0.048	
Benz[a]pyrene	0.57	0.18	0.51	0.11	0.18	0.053	0.038	0.060	0.15	0.018	
Benzo[g,h,i]perylene	0.30	0.01	0.21	0.04	0.10	0.028	0.13	0.11	0.12	0.028	
Indeno[1,2,3-c,d]pyrene	0.32	0.08	0.44	0.01	0.05	0.053	0.012	0.012	0.08	0.026	

Degradation rate of PAHs in Wemeldinge fields

Although fast initial degradation was also expected in the Wemeldinge sediment, the fast degrading fraction is small. The variation in the measured PAHs-concentration is too large to distinguish a fast and slow degrading fraction (Figure 4.6). In this figure the data are fit with one exponential curve. The concentrations at t=0 do not fit in this curve and are (also for all individual PAHs) systematically higher showing the presence of a fast degradable fraction. Therefore it is assumed that, like in Petroleum Harbour sediment, fast degradation lasts one and two years in, respectively, the upper layer of the vegetated field and cultivated field. The following data are fitted with an exponential curve and the resulting actual degradation constants for slow degradation are given in Table 4.3.

One exponential curve is used to fit all of the measured data in the lower layer of the cultivated field. The resulting degradation rate constant is, like in the same Petroleum Harbour field, the constant for fast + slow degradation (k_{f+s}). In the cultivated landfarm the highest degradation rate is obtained. The degradation rate in the vegetated landfarm is slightly slower. The higher values for k_{f+s} also show the presence of a small fast degradable fraction of the lower ring PAHs.

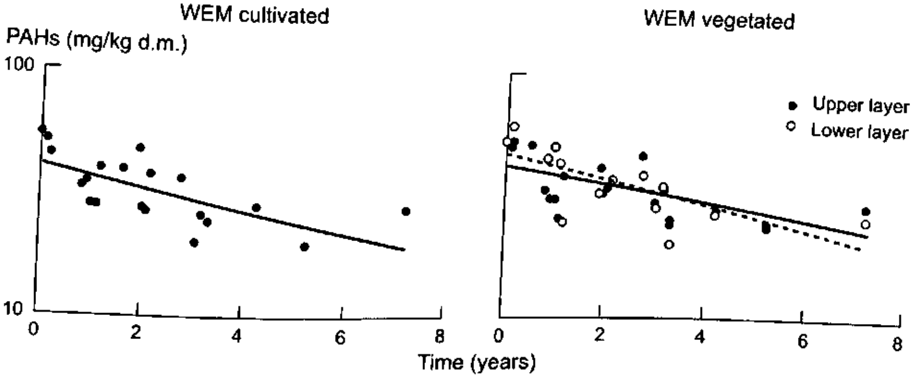

Figure 4.6 PAHs degradation curves in the Wemeldinge landfarms. Data are average concentrations (Dutch National List) per sampling date and are fitted with one exponential curve.

Degree of degradation of individual PAHs in Petroleum Harbour and Wemeldinge sediment

In this long-term experiment it is obvious that all individual PAHs disappear in Petroleum Harbour as well as in Wemeldinge sediment. This is illustrated using the upper layer of the vegetated landfarms, because in this layer the conditions for degradation were most optimal. Figure 4.7 gives the relative concentrations of different degradable fractions of all individual PAHs present in the sediment of the upper layer of the vegetated landfarms. Fast degradable is the amount degraded in the first year, slowly degradable is degraded between 1 and 7 years and very slowly degradable is the residual concentration present after 7 years (this was the situation in 2001). The values are calculated with the obtained fitted curves. The fast degradable fraction has been calculated with the slow degradation curve using a value of t=1

Calculating this value with the fast degradation curve would overestimate the degradation for the lower PAHs.

Very high degradation percentages (fast + slow degradable fractions) are obtained for the smaller PAHs especially in the Petroleum Harbour sediment. The relative residual concentration of the larger PAHs is larger, but these PAHs also decrease in a measurable amount. Compared to the Petroleum Harbour sediment the percentage degraded in the Wemeldinge sediment is lower, but again all PAHs are degraded. Looking to the composition (numbers on top of each column), the contribution of the small PAHs in the original Wemeldinge sediment is much lower, and especially the concentration of fluorene is very low.

After 7 years the concentrations of all individual PAHs have the same order of magnitude (not presented in Figure 4.7). The composition in both landfarmed sediments became comparable.

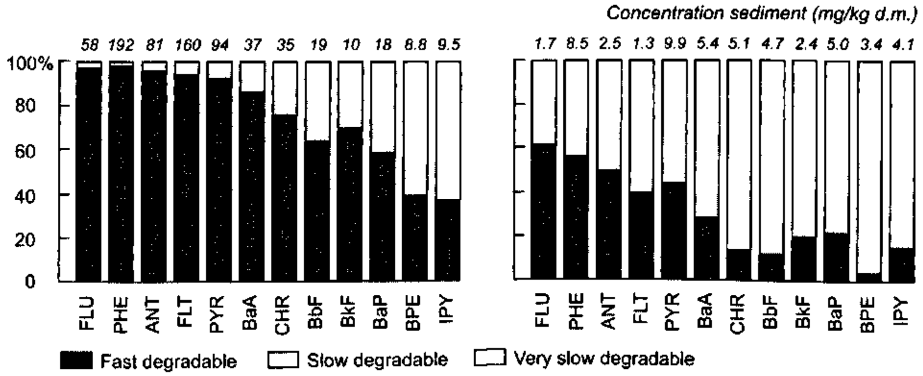

Figure 4.7 Fast, slow and very slow degradable fractions of individual PAHs in Petroleum Harbour (left) and Wemeldinge (right) sediment as measured in upper part of vegetated landfarms. Numbers on top of each column are the concentration in the original sediment (mg/kg d.m.

Degradation rate in Geul Harbour and Zierikzee sediment

In the sediments of Petroleum Harbour and the Wemeldinge Harbour the PAHs-concentrations became stabilised at the end of the measuring period. May be a third very slow degrading fraction should be introduced. Measuring in an additional period will be necessary to establish the proper degradation rate constants for the slow degrading fractions in these sediments. Data from the other two landfarms, Geul Harbour (GH) and Zierikzee (ZZ) can be used to do this. The sediment of these landfarms was treated intensively during three years and passively from 1993 to 2001. The length of this series of data is long enough to derive degradation rate constants. For ZZ the degradation rate is very small. In Figure 4.8 the average PAH-values

(Dutch National List) are presented, including the 95% confidence value for every date of measurement. An issue for discussion is whether it is appropriate to calculate the rate constant from these data. However, it gives an order of magnitude impression. The fitted degradation rate constant (representative for slow + very slow degradation, k_{s+vs}) for the sum of PAH, of the Dutch National List in ZZ equals 0.016 y^{-1}, which is an order of magnitude smaller than the rate constants for slow degradation in the Petroleum Harbour sediment. The accuracy of the individual PAHs is smaller and values are therefore not presented. The curve in Figure 4.8 is an exponential curve; $c_t = c_0 \exp(-kt)$. The curve looks linear, but with small k values and relatively short times the exponential curve can be replaced by the linear function; $c_t = c_0 (1-kt)$.

Although the concentration in GH in year 4 (1994) is already lower compared to ZZ, the relative degradation rate is much higher and fitting the degradation curve becomes more realistic. Even two phases can be distinguished for GH. Figure 4.8 represents the degradation curve of the sum of PAHs of the Dutch National List in GH. 95% confidence intervals are included. The data, also from the individual PAHs, are fitted with two exponential curves representing slow and very slow degradation. Results of fitting are again actual rate constants for slow degradation and the real degradation rate constant for very slow degradation (assuming no extreme slow degradable fraction is present). The degradation rate constants are given in Table 4.3. The rate constants for slow degradation are comparable with the values for slow degradation in the Petroleum Harbour sediment and the values presented for Wemeldinge sediment.

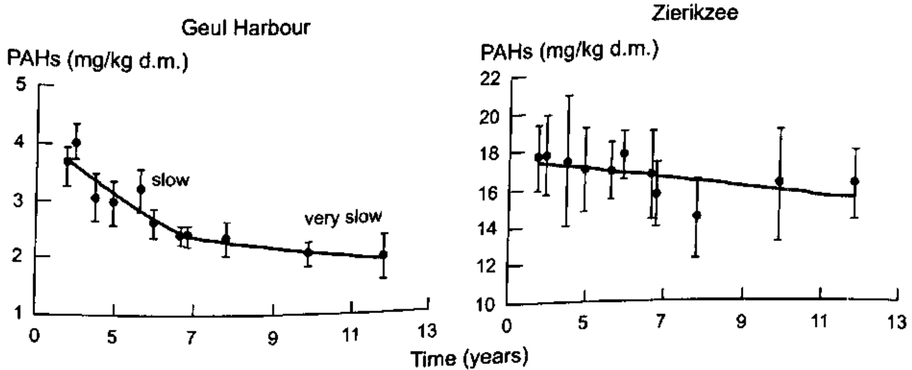

Figure 4.8 PAHs (Dutch National List) degradation in Geul Harbour and Zierikzee sediment. Degradation curve are fitted with exponential curves.
The average values of Geul Harbour are based on respectively 19; 18; 18; 18; 10; 9; 9; 9; 10; 5 and 5 samples. For Zierikzee they are based on respectively 19; 19; 18; 28; 10; 8; 13; 14; 10; 5 and 5analysed samples. 95% confidence values are given.

4.3.2 Desorption of PAHs

Tenax experiments to study desorption were described in the year 1997 by Cornelissen *et al.* (1997). These measurements were applied on the sediments in Kreekraksluizen from 1997. Fortunately the original sediments of the Petroleum Harbour and the Wemeldinge Harbour have been stored under anaerobic conditions and still contain the original concentration of PAHs. The additional three years of ageing of the sediment will be small compared to the age of the pollution in the sediment ranging from tenths of years in the Wemeldinge sediment to more than 50 years in the Petroleum Harbour sediment. The original Petroleum Harbour sediment contained the highest amount of PAHs (550 mg/kg d.m.) and gave the most reliable results using the Tenax-method. The original sediment and sediment on the cultivated Petroleum harbour sediment has been analysed in 5-fold. An example of the desorption curve of phenanthrene in both samples is given in Figure 4.9. The first drop is representative for the fast desorbing fraction and the second part for the slow desorbing fraction. Because no re-adsorption takes place (surplus of Tenax) and the duration of the experiment is small compared to the period of ageing of the sediment, desorption is the only process to be considered. The multi-compartment model can be used and the data are fitted with a two compartment model. Using curve fitting it is possible to calculate the fast desorbing fraction and the rate constants for fast and slow desorption. Results for all individual PAHs and standard deviations are given in Table 4.4. The rate constant for fast desorption is the one that can be used in the multi-compartment model. Because the presence of a very slow desorbing fraction is not taken into account, the values for rate constants of the slow desorbing fraction have to be considered as the actual value.

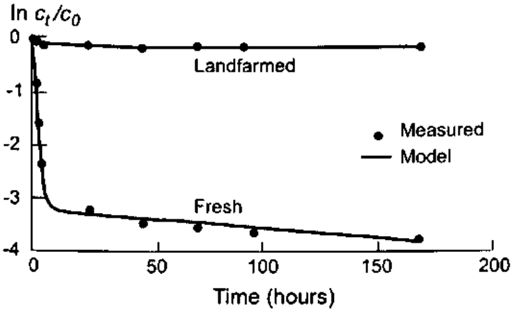

Figure 4.9 The desoption curve of phenanthrene in fresh and landfarmed Petroleum Harbour sediment measured with the Tenax-method. Relative concentration in the sediment c_t/c_0 as function of time. Measured data and fitted curve (two-compartment model).

Table 4.4 Fast desorbing fraction and the desorption rate constants k_{fast} and k_{slow} in fresh and cultivated (1997) sediment of Petroleum Harbour. ( ) = standard deviation (n = 5).

PAHs	Fresh sediment						Cultivated sediment					
	Fraction fast (%)		k_{fast} (y^{-1})		k_{slow} (y^{-1})		Fraction fast (%)		k_{fast} (y^{-1})		k_{slow} (y^{-1})	
Fluorene	85	(3)	10237	(2556)	42	(7)	5	(3)	1545	(1357)	3.9	(2.0)
Phenanthrene	90	(5)	6701	(980)	33	(2)	18	(12)	2103	(1792)	9.7	(5.1)
Anthracene	88	(4)	6246	(798)	38	(7)	11	(11)	3558	(3191)	4.8	(2.6)
Fluoranthene	86	(5)	2686	(443)	83	(17)	9	(3)	2204	(2709)	6.9	(3.9)
Pyrene	75	(3)	701	(156)	22	(7)	7	(5)	1550	(1936)	9.9	(5.8)
Benz[a]anthracene	76	(3)	426	(84)	25	(8)	6	(3)	793	(374)	1.9	(1.3)
Chrysene	76	(5)	426	(99)	17	(13)	7	(6)	1198	(827)	2.9	(1.4)
Benz[b]fluoranthene	59	(11)	262	(33)	37	(11)	19	(8)	337	(211)	5.1	(4.3)
Benz[k]fluoranthene	54	(12)	268	(29)	40	(11)	13	(8)	629	(587)	7.1	(3.7)
Benz[a]pyrene	55	(14)	231	(38)	31	(12)	28	(9)	197	(52)	6.7	(4.3)
Benzo[g,h,i]perylene	28	(4)	3022	(176)	21	(3)	4		461	(918)	10.8	(12.8)
Indeno[1,2,3-c,d]pyrene	19	(4)	3476	(866)	30	(6)	11		61	(52)	1.2	(0.8)
Average	66	(6)	2890	(521)	35	(9)	11	(7)	1220	(1168)	5.9	(4.0)

There is a logical order in the size of the fast fraction and in the values of k_{fast} in the fresh sediment (except for the underlined values). There is no explanation found for these high underlined measured values. The smallest ring PAHs (with the highest water solubilities) have the highest values. Degradation of the fast fraction results in a shift in the composition of the PAHs. In the treated sediment the fast fraction is much smaller and no significant differences are present between individual PAHs. Due to the lower concentration in the cultivated sediment and the lower fast desorbing fraction, the accuracy of the Tenax-method is lower as is shown by the standard deviation. The standard deviation for the fast desorbing fraction in the cultivated sediment is of the same magnitude, which means a relative standard deviation of 50 to 100%. The standard deviations for k_{fast} and k_{slow} in the treated sediment have also the same magnitude as the values itself. This has to be kept in mind when evaluating the results. Generalised, if the fast desorbing fraction is low (< 25%), the relative standard deviation is about 50 to 100 %. Comparable results for the fast fractions in fresh sediment were obtained by Cornelissen *et al.* (1998) in Petroleum Harbour sediment (not the same dredging). After treatment in a bioreactor, the available fractions became comparable with the results from the cultivated landfarm or were higher as measured in sediment from a less effective bioreactor.

The desorption constant for slow desorption k_{slow} does not depend on the number of rings of the PAHs or on the octanol-water distribution constant (K_{ow}) of the PAHs (see Table 2.1 in Chapter 2). This has also been reported by Kan *et al.* (2000) studying chlorinated compounds.

Table 4.5 Fast desorbing fractions of individual PAHs and the average desorption rate constants in fresh and treated sediments sampled October 1997. ( ) and [ ] results of respectively Cornelissen *et al.* (1998) and Cornelissen *et al.* (2000-a) in the same sediment.

	PH				WEM			GH	ZZ
	Fresh	Vegetated lower '97	Vegetated upper '97	cultivated '97	Fresh	Vegetated lower '97	Vegetated upper '97	'97	'97
PAH-total Dutch National List on moment Tenax measurement (mg/kg d.m).	550	120	45	35	45	30	30	2	15
Fraction fast available PAH (%)									
Fluorene	85	20	2	5	27 (27) [26]	32	6 (7)	10	13
Phenanthrene	90	26	6	13	26 (20) [12]	20	7 (5)	9	10
Anthracene	88	52	3	5	42 (38)[26]	25	9 (5)		4
Fluoranthene	86	65	18	9	14 (32) [30]	21	7 (9)	2	2
Pyrene	75	67	25	7	32 (38) [31]	13	3 (12)		2
Benz[a]anthracene	76	60	21	6	23 (21) [17]	5	2 (8)	6	1
Chrysene	76	58	14	8	19 (18) [16]	7	3 (10)	4	2
Benz[b]fluoranthene	59	58	28	19	7 (16) [12]	4	3 (13)	2	3
Benz[k]fluoranthene	54	72	23	13	13 (15) [11]	4	2 (10)	4	2
Benz[a]pyrene	55	72	24	31	8 (14) [8]	3	4 (11)	5	2
Benzo[g,h,i]perylene	28	2	1	4	6 (8)	6	3 (15)	11	-
Indeno[1,2,3-c,d]pyrene	19	1		11	10 (18)	1	3 (25)	4	5
Desorption rate constant *k*. Average value for all PAHs (y^{-1})									
k_{fast}	2890	2570	1190	1220	2220	3400	1270	5870	3190
k_{slow}	35	10.7	5.9	5.9	12.7	5.4	3.2	3.8	11.4

The availability for desorption in the other sediments is much lower. Results are given in Table 4.5. The individual values in Petroleum Harbour sediments showed that depending on the PAH-concentration present (fresh > vegetated lower > vegetated upper = cultivated) the highest for desorption available fraction shifted from the light PAHs to heavy PAHs. In the most degraded sediments the availabilities for desorption are reduced to 10 to 20%. The shift to more heavy PAHs is not visible in de Wemeldinge sediments.

For the fresh sediment, results of Cornelissen *et al.* (1998 and 2000-a) are also presented. They have analysed the same sediment. The slightly enlarged availabilities for desorption in the fresh Wemeldinge sediment reduce to values below 10 % in the treated sediments, which is comparable with the sediments from the Geul Harbour and Zierikzee. Comparison of the measured values with the values of Cornelissen shows that all of the Tenax-values are comparable, taking into account a standard deviation of about 7 as given in Table 4.4.

The desorption rate constants are only presented as average values for all PAHs, because of the high standard deviation at lower concentrations. All the desorption rate constants have the same order of magnitude. The presented desorption rate constants are also in agreement with observations of Cornelissen *et al.* (1997), Johnson *et al.* (2001). Only k_{slow} in the fresh Petroleum Harbour sediment is higher. This may be caused by the presence of a high amount of mineral oil. This oil acts as extra phase which extracts the PAHs from the soil. Diffusion through this liquid phase will be fast.

Because of the limited accuracy of the Tenax-method at small fractions available for fast desorption, the elaborated procedure was not repeated in the following years (1999 and 2001). Tenax-measurements were restricted to the amount desorbing in 6 hours. Cornelissen *et al.* (2001) stated that this amount could also be used as an estimate for the fast desorbing fraction. Using the average value for k_{fast} measured in this study (see Table 4.6) of 3000 y^{-1}, it can be calculated that 88% of the fast desorbing fraction has been desorbed in these 6 hours. In desorption experiments of 1999 and 2001, several outliers were measured and the relative standard deviation was high. Results indicate that the fast desorbing fractions measured with Tenax in 1999 and 2001 were low (below or far below 10%) as illustrated with the median value of the measured fractions (Figure 4.10). For the lower layer of the vegetated Wemeldinge sediment the fraction available for fast desorption decreases from 1999 to 2001. Differences for the other sediments are within the error of measurement. Very low are the fractions available for fast desorption in the fully aerobic Wemeldinge sediments (cultivated and vegetated upper) and the Zierikzee sediment.

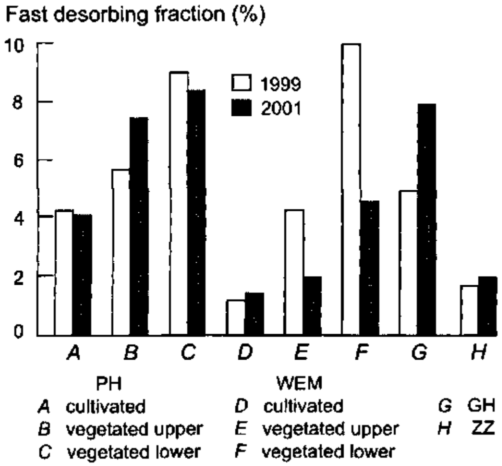

Figure 4.10 Fast desorbing fractions (%) measured with the Tenax method (6 hours procedure). Median values for all measured PAHs are presented.

Taking into account the relatively high uncertainty of the measurements at low availability for desorption, the following pattern can be recognized:

- The fast desorbing fraction was only high in the original sediments (Table 4.6) and remains low in the treated aerobic sediments (Figure 4.10).
- The highest values are present in the layer with the smallest degradation (lower layer of vegetated landfarms)
- Even in sediments that are bioremediated for 12 years (Geul Harbour and Zierikzee) there is still a fast available fraction that is measurable.

4.3.3 Decomposition of organic matter

In the Petroleum Harbour sediment the original sediment had an organic matter content (measured as loss of ignition) of 12%. This percentage decreased in the cultivated landfarm to 7% (standard deviation, s.d. 1%) within 1 year. In the upper layer of the vegetated landfarm the organic matter content stabilized at 8% (s.d. 1%) and this percentage was attained within 2 years. In the lower layer a stable 8% was attained within 4 years. In the Wemeldinge sediment the organic matter content decreased from 9% to 5% (s.d. 0.8%) in the cultivated landfarm and to 6% (s.d. 0.8%) in the vegetated landfarm. The latter percentage was attained in 1 and 4 years in, respectively, the upper and lower layer.

The results of the organic matter content for the passive treated sediments GH en ZZ are given in Figure 4.11. During passive landfarming there is no further reduction of organic matter. It should be realised that the fields were covered with vegetation and that the organic matter of the vegetation (both root and shoot) compensates for a decrease of organic matter. The dynamic nature of the organic matter is too large to give a pronouncement on the degradation of the original organic matter. Remarkable is the decrease of the standard deviation. This shows that the soil life is active and a homogenous distributed organic matter is created in a period of 5 to 10 years. This is in agreement with the rate constants identified in Table 2.5 (Chapter 2) and these values are further used in the discussion.

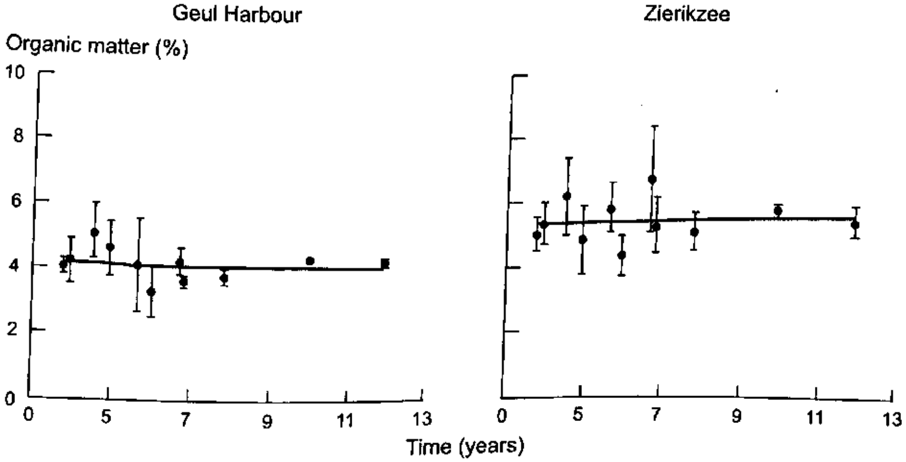

Figure 4.11 Organic matter (measured as loss of ignition) (%) in Geul Harbour and Zierikzee sediment. Bars represent the standard deviation.

4.4 Discussion

Summarising the degradation of PAHs in the different sediments (4.3.1), three degradation rates can be distinguished; (1) fast, (2) slow and (3) very slow degradation. The sizes of the different fractions belonging to these rates vary. The fast degrading fraction can be degraded in the first year. In this period however, oxygen is the limiting factor. It is first necessary to dewater the sediment and water filled pores have to be replaced by air filled pores. If oxygen is limiting during several years, a fast degrading fraction is not recognised as shown in the lower layer of the vegetated landfarms. In Petroleum Harbour landfarm a high fast degrading fraction can be easily recognised. In the passive Geul Harbour landfarm a very slow degrading fraction could be recognized after 7 years of landfarming. This was not possible in the Zierikzee landfarm and the other landfarms were still too young.

4.4.1 Degradation and desorption

Prediction of the degree of degradation

As explained in Chapter 3, Tenax can be used as a tool to measure the fraction available for biodegradation. With Tenax the fast desorbing fraction is measured. Figure 4.12 gives the relation between the degradable fraction (degraded in one year of landfarming) and the fast desorbing fraction of the individual PAHs in Petroleum Harbour sediment. The values for the amount degraded in one year are derived from Figure 4.7. A similar figure has been presented by Cornelissen *et al.* (1998) and can be constructed using other methods predicting the for degradation available fraction (see Chapter 3).

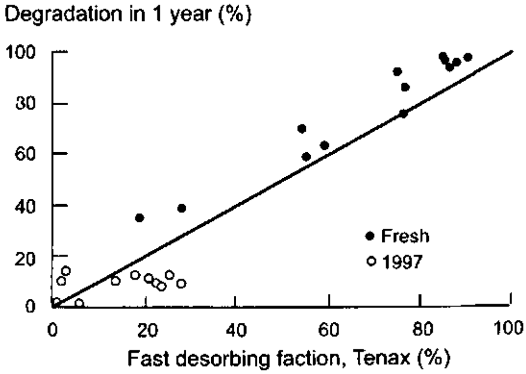

Figure 4.12 PAHs, percentage degraded on the landfarm Kreekraksluizen in one year versus percentage fast desorbing fraction (Tenax-measurement). The solid line is the line with slope =1.

In the fresh sediment, the degradation is larger than that predicted using Tenax. In the first year, however, also part of the slow available fraction has been degraded, which increases the percentage degraded. Tenax gives an estimate of the fast desorbing fraction and excludes the slow desorbing fraction.

Kinetics of degradation and desorption

Using the Tenax method, it is also possible to establish kinetic parameters. Cornelissen *et al.* (1998) found that desorption rate constants measured with Tenax were comparable with degradation rate constants in a bioreactor. In an experiment were artificial polluted soil was shaken in vials, Braida *et al.* (2000) found almost the same curves for desorption and degradation. Desorption was measured using Tenax and biodegradation was measured following $^{14}CO_2$ release of the degraded phenanthrene. The 'polluted' soil was equilibrated during 180 days. In both cases slurry systems were used for measurement of desorption and for degradation. They show that comparing results of experiments, good correlations will be obtained with experiments having the same set-up and timeframe.

Comparing the degradation rate constants found on the landfarm (Table 4.3) with the desorption rate constants measured on the laboratory (Table 4.4), large differences are observed. In Table 4.6 the magnitude of the values are presented. Some values are marked as actual and in comparing, actual values have to be compared with actual values. For the very slow desorption rate constant, values from literature have been evaluated (Ten Hulcher *et al.*, 1999, Johnson *et al.*, 2001). Their values for very slow desorption are a factor 8 to 66 smaller than the values for slow desorption. In model sorbents, which are more simple compared to sediments Cornelissen *et al.* (1998) found that very slow desorption rates constants were approximately a factor 10 smaller. For other organic compounds (trichloroethylene, 1,3-dichlorobenzene and 1,2,4-trochlorobenzene) the same research group (Cornelissen *et al.*, 2000-b) showed differences between slow and very slow desorption constants of a factor 25 to 66. Van Noort *et al.* (2003) reported differences between slow and very slow desorption of a factor 100. In Table 4.6 a value for the very slow desorption constant of 0.1 - 0.3 y^{-1} has been used which is a factor 23 to 69 smaller than the rate constant for slow desorption.

May be it is even necessary to add extreme slow desorption and degradation. Especially for those PAHs that are often adsorbed in coal derived particles. Using Thermal Program Desorption, Gosh *et al.*, 2001 reported desorption rate constants for PAHs adsorbed in coal derived particles and with molecular weights of 178, 202, 228 and 252 of, respectively, 0.029, 0.007, 0.006 and 0.002 y^{-1}. These values are not presented in the table, because it was not possible to recognise an extreme slow degradable fraction on the landfarm. The accuracy of the measured PAH-concentrations is too low and a monitoring period, much longer than described in this chapter will be necessary to derive a rate constant.

Using results of Smith *et al.* (2001) actual slow degradation constants between 0.12 an 0.17 y^{-1} can be calculated during a period of passive landfarming (2-6 years after the start of the landfarm). These values are comparable with the values presented in Table 4.3 and 4.6.

Table 4.6 Rate constants for degradation of PAHs in a landfarm and desorption of PAHs measured with Tenax (Expressed in y-1).

Rate constant	Degradation (landfarm)	Desorption (Tenax)
k_{fast}	>3	2600
k_{slow}	0.33	
k_{slow} actual	0.15	6.9
$k_{very\ slow}$	0.03	0.1-0.3

On first sight, desorption rate constants presented in Table 4.6 do not explain the rate of degradation. This is logical for the fast degrading fraction. As long as there are other limiting conditions (absence of oxygen), the supply of oxygen will explain the degradation rate.

During slow degradation, oxygen is not limiting degradation, because the sediments were dewatered and completely aerobic. Comparing the rate constants it is important to realise the differences in experimental conditions. In the landfarm, the soil is unsaturated with water, providing aerobic conditions. The Tenax-system is a slurry system and no gas-filled pores are present. Diffusion to the Tenax, which is the driving process for desorption is faster in a fully water saturated system and also when soil particles (aggregates) are smaller. In a non-saturated landfarm, diffusion to the degrading organism will be slower. As shown in Chapter 2, the rate constant k (Equation 4.2) is proportional to the square of the moisture content (θ, expressed in m^3/m^3) and inversed proportional to the square of the radius (r in m) of the soil aggregate. It also depends on the pore volume in the aggregate (ε in m^3/m^3).

$$k \sim \frac{\theta^2}{(1-\varepsilon)r^2} \tag{4.2}$$

For biodegradation oxygen is necessary and the supply is optimal in a landfarm, if about 25% or less of the total sediment/soil volume is filled with water. Depending on the soil type, the moisture content in the aggregates is higher. In the fresh sediment the fraction of the pore volume is about 0.7, which is completely filled with water. Comparing sediment treated on the landfarm with a pore volume fraction of 0.55 and a range of water filled soil volume of 0.2 to 0.5 in the landfarm with the fresh sediment, a difference of 3 to 18 in the rate constant k can be calculated. In the Tenax measurement the aggregates are partly broken up and are free rotating. This influences the aggregate radius. If this is a factor 2, differences in the rate constant between 12 and 76 can be explained. Due to the different experimental conditions in the landfarm and the Tenax-experiments the difference (Table 4.6) between the rate constants for slow desorption and slow degradation (both are presented as actual) is now understandable. For the very slow process the difference is less clear (data for very slow degradation are based on only one treated sediment) and both rate constants differs a factor between 10 and 30, which fits in the previous explanation. The smaller difference may also indicate that diffusion is not the only process explaining degradation and also other processes like degradation of organic matter should be considered (see 4.4.2).

In the fresh Petroleum Harbour sediment actual desorption rate constants are a factor of 2 to 6 higher than in the treated sediment (Table 4.5). An explanation for this difference is the high mineral oil content in this sediment. This acts as an extractant and increases the rates of desorption. Already in the first year there is a large decrease in the mineral oil content, which reduces the extracting power of the mineral oil present.

To be able to use the three compartments model for prediction of degradation, rate constants must all be related to their fraction. This will increase the value of the actual values. This is not important for the fast degrading fraction, because the degradation rate constant can be much larger depending on the rate of dewatering. In addition, the fast available fraction in Petroleum Harbour sediment is already large. Correction of the actual value is important for the slow degradable fraction. This value will be larger if a large part of the residual fraction is very slowly degradable. If it is assumed that after 7 years 90 % of the slow available fraction has been degraded, the values of the rate constant of the slow degradable fraction in the different sediments will have a value of 0.33 year^{-1}.

Desorption rate constants presented for fast desorption follow a logical order of high rate constants for the low molecular PAHs and low rate constants for the high molecular ones. The differences are however relative small, showing that Dissolved Organic Matter (DOM) plays a role in the desorption process (see Chapter 2 Figure 2.2). This figure showed that the differences between diffusion constants of individual PAHs became smaller with increasing DOM. In the landfarm the differences between the individual PAHs for the degradation rate constant are even much smaller. Desorption, however, will still be an important step in the degradation process, because the fraction available for fast desorption measured with Tenax correlates very well with the amount degraded. On the landfarm the supply of oxygen (dewatering) seems to be the rate determining process at the start of landfarming sediments and overshadows the desorption process.

DOM must also be important in the rate of desorption and degradation of the slow and very slow fractions, because it is not possible to differentiate between the different PAHs. If it was possible to differentiate between different PAHs with the rate of desorption, there should be another mechanism for degradation of the slow and very slow degradable fractions. The desorption process seems to be the limiting process for degradation. This is, however, not a full proof; degradation of the organic matter may give the same results (see 4.4.2).

Prediction of degradation rate from the measured for desorption available fraction

Most methods for the measurement of those PAHs identified as 'for biodegradation available PAHs' only estimate this available fraction and not the kinetic parameters (see also Chapter 3). If kinetic parameters are estimated additional measurements are necessary which makes it expensive for more routine applications. It would be an improvement if the time necessary for biodegradation on a landfarm could be predicted from the measured available fraction.

Using the first order degradation function, the actual degradation rate constant can be calculated from the amount degraded in one year or from the fast available fraction measured with the Tenax-method. This theoretical relation is plotted with a solid line in Figure 4.13. In the same figure the actual degradation rate constants in 1997 (Table 4.3) have been plotted against the in 1997 measured fractions available for fast desorption (Table 4.5). The values originate from different treated sediments and the fresh Petroleum Harbour sediment in the upper layer of the vegetated landfarm.

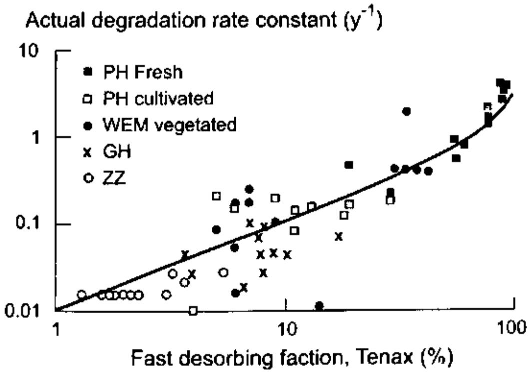

Figure 4.13 Actual degradation rate constant as function of the fast available fraction.
- Calculated (solid line).
- Measured in different sediments in 1997, degraded in 1997 versus fast desorbing fraction (Tenax method) (points).

Within the inaccuracy of the Tenax-method at low fast desorbing fractions and also taking into account the low 'fraction available for fast desorption' measured in 1999 and 2001, three ranges can be distinguished:

- **Very slow degradation.** Fractions available for fast desorption of most individual PAHs between 0 and 10%.
- **Slow degradation.** Fractions available for fast desorption of most individual PAHs between 5 and 25%.
- **Fast degradation.** Fractions available for fast desorption of most individual PAHs between 25 and 100%.

Knowing the similarity in results with other methods that are used to predict the degradable fraction, the prediction can also be used to predict the degradation rate.

4.4.2 Degradation of PAHs and organic matter

The desorption process as measured with the Tenax procedure is a good method for the explanation for degradation if all other conditions are constant during the whole landfarming period. This generally is not what occurs. Already in the first year a considerable amount of organic matter has been degraded. This reduces the number of sorption sites. The influence of the degradation of organic matter during dewatering, on the degradation rate of PAHs of the fast degrading fraction cannot be quantified. There are more influencing factors, aeration and desorption, but also formation of new organic matter (root residuals). It is not possible to distinguish between all these factors. Talking in terms of glassy and rubber-like organic matter it seems plausible that the rubber-like organic matter is degraded during dewatering. If the degradation of the organic matter was the dominant process, the degradation rate of PAHs should be independent of the size, because all PAHs should become available in the same rate. This is not observed, showing that the degradation rate of the fast fraction is diffusion driven.

After the first dewatering period the organic matter content seems to be constant. There is however a constant degradation of old organic matter and formation of new organic matter in biologically active soil. In this period rate constant for the degradation of organic matter are valid between 0.005 and 0.25 y^{-1} (see Table 2.5 in Chapter 2). These values are of the same magnitude as found for the slow and very slow degradation. Reemtsma *et al.* (2003) could not prove but found it likely that the turnover of organic matter is linked to the release of aged contaminants. If degradation of the organic matter (the adsorption sites) is responsible for the degradation rate, it should not be possible to distinguish between the different PAHs. All sorption sites are degraded with the same rate, independent of the adsorbed PAHs. This has also been found during the slow and very slow degradation; all PAHs degrade with a rate constant of the same magnitude. As mentioned in 4.1 the same can be predicted from the theoretical model described in Chapter 2 taking into account the effect of the association of PAHs with dissolved organic matter.

It is stated, however, that degradation rate constants of PAHs and organic matter have the same order of magnitude. Therefore it is not physically realistic anymore to describe the slow degradation only with a diffusion process. The organic matrix is not stable within the timeframe of about 10 years. In a mathematical description of the slow degradation, the dynamics of the organic matter turnover should be included. However, changes in organic matter will not automatically lead to degradation. It is also imaginable that a change of organic matter will lead to a better inclusion of the PAH molecule, which also can be described with the term bound residue.

4.5 Conclusions

In this long-term landfarming experiment, it was possible to distinguish between different rates of degradation; a fast degradation during dewatering, a slow degradation in the first period of about 7 years and a very slow degradation after the period of slow degradation. This pattern can be recognised for all individual PAHs. Not only small PAHs are degraded on the used passive landfarm, but also the larger 5 and 6 ring PAHs. For the fast degradable fraction, the oxygen supply is the limiting factor. As a result of natural dewatering the degradation of the fast degrading fraction occurs in the first 1-2 years in a landfarm. In thick layers of sediment the oxygen limitation may cause even longer delays as shown in not cultivated layer sediment of about one meter.

The fractions available for fast desorption measured with the Tenax-method provide a good estimate for the degradation in the following year on the landfarm. It is even possible to predict the degradation rate from the measured for fast desorption available fraction.

Desorption rates (diffusion from a soil aggregate to the water phase followed by adsorption on an adsorbing agent) measured with the Tenax-method were much faster than the degradation rate observed on the landfarm. Taking into account the lower moisture content and lower pore volume in a landfarm compared to the slurry during the Tenax-measurement and differences in the radius of the soil aggregates, differences in observed rate constants for slow desorption and degradation can be explained. Desorption as a result of a diffusion process can therefore be used to explain degradation on a landfarm. Increasing the moisture content and decreasing the particle size may increase the diffusion and degradation rate. This is, however, not a realistic option for landfarming. High moisture content will limit the necessary diffusion of air into the landfarm and cultivation will not lead to the very small particles necessary. If a high degradation rate is necessary, it is better to use the more expensive slurry systems with active introduction of oxygen. These slurry systems (bioreactors) are not the subject of this thesis.

Diffusion limited desorption of PAHs is not the only limiting factor in the landfarm for explaining slow degradation. A second explanation for especially the very slow degradation is the dynamics of the organic matter in the sediment and created soil. During dewatering there is also a decrease in organic matter that is easily degradable organic matter and is probably the rubber-like organic matter. The remaining organic matter is more stable (glassy) and desorption from this organic matter will occur more slowly. Also, this organic matter will be decomposed and the rate of this decomposition has the same magnitude as the rate of slow and very slow degradation. This indicates that the organic matter dynamics may play a role in degradation.

Using a three compartment model (Equation 4.1), the degradation can be described with the sizes of the fast, slow and very slow fraction and their degradation rate constants of respectively >3.5: 0.33 and 0.04 y^{-1}. Using these constants the following fractions can be distinguished with corresponding degradation times:

- **Fast degradable fraction**: more than 90% will be degraded in one year of landfarming, provided that proper conditions for degradation are managed and maintained.
- **Slow degradable fraction**: about 7 years are necessary to remove 90% of this fraction.
- **Very slow degradable fraction**: even 13 years are insufficient for accurate measurement of this degradation rate, and 30-60 years may be necessary for 90% degradation.

Depending on the distribution of PAHs between the different degradable fractions, short and/or long periods may be necessary to reach target values set for remediation. Returning to the three compartment model, it is now possible to fill in 4 of 6 unknown parameters. Values of the degradation rate constants are presented in this chapter and the fast degrading fraction can be established using the Tenax-method or another method to establish the fraction available for fast biodegradation. There is one unknown remaining, because the sum of all the fractions is 1. If it is possible to measure one of the other fractions, it becomes possible to predict the degradation curve. Possible methods are:

- A desorption method like Tenax during a period necessary to desorb 90% of the slow desorbing fraction (40 days if k_{slow} for desorption is 20).
- A desorption method at increased temperature, which makes shorter extraction periods possible, like the method (desorption at 60 °C) suggested by Cornelissen *et al.* (1997). Desorption during about 30 hours will be sufficient).
- Measurement of the very slow available fraction, by destroying the organic matter associated with the slow desorbing fraction. This comparable with the persulphate method of Cuypers (2001).

Currently, the landfarms at Kreekraksluizen are stable systems and the degradation will continue in the coming years, improving the quality of the sediment. If degradation of organic matter is the explaining factor for slow and very slow degradation, it could be concluded that the degradation rate could be increased by stimulation of the degradation of the organic matter. This will probably give lower residual concentrations, but is not a wise decision. Organic matter acts as an adsorption site for PAHs. A strongly adsorbed PAH will not be responsible for negative effects on the eco-system. By removing the organic matter the concentration of PAHs may drop more rapidly, but removal of organic matter may also increase the risks. It is better to conclude that an active soil system may increases the degradation rate of PAHs. In an active soil system there is a high turnover of organic matter. Old organic matter is degraded and new organic matter is created from residuals of vegetation. By degradation of the old organic matter the degradation rate of PAHs may increase. The new organic matter creates new sorption sites, which may prevent that non-degraded PAHs become available for soil organisms. Presences of roots of vegetation and worms do not only play a role in the organic matter turn over, but also on the size of the aggregates. Decreasing of aggregate size to smaller than 1 mm (see Chapter 2) may effect an increase of the desorption rate.

5 Degradation of mineral oil in landfarmed sediments

5.1 Introduction

Mineral oil is one of the most commonly occurring organic contaminants in sediments. It is persistent in sediments due to the existence of anaerobic conditions. Under aerobic conditions found in a landfarm, mineral oil in sediments and soil is biodegradable, as has been described in Chapter 1 and 2. There is already a long tradition (Aora *et al.*, 1982) of successful treatment of terrestrial soils polluted with mineral oil products, as has been summarized in Chapter 1. Several companies are active in the treatment of mineral oil polluted soil in open and covered landfarms. Even under arctic conditions (Prince and Bragg, 1997; Whyte *et al.*, 1999), mineral oil can be degraded.

One should expect comparable results with bioremediation of sediments. There are, however, differences between oil-polluted sediments and oil-polluted soils. Although sediments are changed into soils during landfarming, differences in conditions at the beginning of treatment will influence the degradation rate. The degradation of mineral oil is mostly expressed as a decrease in the total concentration. Mineral oil content is not one unique chemical but a complex mixture of individual compounds. As discussed previously in Chapter 3, mineral oil in sediments is present in different physical forms (Harmsen and Zweers, 2000; Brils *et al.*, 2002):

- Free occurring un-bound droplets.
- Droplets bound to sediment particles.
- Mineral oil adsorbed on the surface of organic matter.
- Mineral oil absorbed in the organic matter.
- Mineral oil present between mineral particles.

There is no technique available that measures the entire range of compounds present in all mineral oil products (Farrell-Jones, 2003). A reported mineral oil concentration is therefore defined by the analytical method used, and it can be difficult or impossible to compare results of different analytical methods. In this thesis, a gas chromatographic method was used, and the concentrations reported consist of all the hydrocarbons extracted with a mixture of acetone and petroleum ether, still present after a clean-up of the extract with florisil and visible in the gas chromatogram between C_{10} and C_{40} (NEN 5733; ISO 16703). Clean-up is necessary to remove co-extracted natural organic matter. Use of other extraction methods and clean-up methods may result in higher, but also lower concentrations (Harmsen and Zweers, 2000).

Measuring a product, originated from crude oil, gives an oil chromatogram that consists of an unresolved hump with spikes on top. The spikes are recognised as n-alkanes (upper chromatogram Figure 5-1). Light or low boiling oil compounds, in this example originating from gas oil, are shown in the left part of the chromatogram, and heavy oil compounds containing larger alkanes from lubricant oils are shown in the right part. If mineral oil is introduced into anaerobic soil, it can be detected even after a long period. If degradation does occurs, the easily degradable n-alkanes will be removed first (Atlas, 1984; De Jonge; 1996; Pond *et al.*, 2002), and the mineral oil remaining is called a weathered mineral oil.

The typical mineral oil pattern that is found in polluted soils is not seen in sediments. The reason for this is logical. The density of spilled oil is usually lower than the density of water; oil, therefore, will float on water and tends not to go into the sediment. Exceptions are some greases or special oil products, but these products are not released into the environment in large amounts. Due to evaporation the most volatile compounds will disappear quickly. Movement of the water is responsible for presence of suspended particles in the water and break up of the oil film in the water. Oil particles will adsorb to the solid particles and settle out together with these particles. The water layer above the sediment, including the top layer of the sediment, is aerobic and can be considered a bioreactor. The easily degradable compounds are partly removed in this layer. The easily degradable low boiling compounds and the n-alkanes are visible at the beginning of the upper chromatogram in Figure 5.1. The remaining in the sediment is weathered oil (second and third chromatograms in Figure 5-1); weathered oils are also present in a polluted terrestrial soil after a period of active bioremediation. The amount of oil components visible in the beginning of the chromatogram is low.

The Dutch target value for mineral oil in sediment (C_{10}-C_{40}) after remediation is a total concentration; 50 mg/kg d.m for multifunctional use as soil and 500 mg/kg d.m for reuse as building material; the latter value has changed to 2000 mg/kg d.m in 2004; see also Chapter 1. As mentioned previously, mineral oil consists of a large number of individual compounds, having different boiling points, volatilities, and also different polarities, resulting in different solubilities in water. In a study on toxicity of mineral oil in marine sediments, it has been shown that the toxicity for *Vibrio Fisheri*, *Corophium Volutator*, and *Echinocardium Cordatum* does not correlate with the total concentration but strongly correlates with the lower boiling points, especially to those within the C_{10}-C_{19} range (Brils *et al.*, 2002). These are also the components that are first degraded, as seen by comparing the chromatograms of the sediments in Figure 5.1.

The interaction of mineral oil and sediment particles and especially the organic matter may be responsible for a low bioavailability, as described in Chapter 3. The low availability combined with the weathered character of mineral oil in sediment (the easily degradable components are already removed) can be responsible for a degradation rate slower than normally found with landfarming of oil polluted terrestrial soils. The degradation rates of mineral oil in sediment treated on the landfarm Kreekraksluizen are described in this chapter. The same sediments as described in the previous chapter on PAHs degradation were investigated, i.e., sediments from Petroleum Harbour, Wemeldinge, Geul Harbour and Zierikzee. Degradation rates based on first order degradation are also derived in a comparable way. This chapter is limited to degradation rates and does not include desorption rates, because, unlike PAHs, it was not possible to correlate desorption, as measured using Tenax, with degradation data. It can also be discussed whether desorption of mineral oil molecules adsorbed on organic matter is the most important process for biodegradation. Mineral oil is also present as droplets, for which dissolving is more important to become available for degradation, and on which surface micro-organisms can be active. If mineral oil is absorbed within organic matter, the degradation of organic matter may be the rate-explaining factor for biodegradation.

Comparable with the degradation of PAHs described in the previous chapter, different degradable mineral oil fractions were distinguished: (1) fast, (2) slow and (3) very slow. Although it was not possible to predict the fast degradable fraction, as was possible for PAHs, and to establish the mechanisms important for transport of non-available mineral oil to active degrading organisms, degradation rates of the fast and slow degradable fractions could be measured and are presented in this chapter. All sediments treated on the landfarm Kreekraksluizen were used for this study. Knowing the degradation rates for mineral oil, predictions are made of the time necessary to reach target values for reuse. The time necessary for treatment on a landfarm is an important component of the treatment strategy.

5.2 Materials and methods

The investigation of the degradation of mineral oil has been conducted on the same experimental landfarm on Kreekralsluizen as used for the study of PAHs degradation (Chapter 4). On this landfarm, sediments from the Geul Harbour (GH) and the harbour of Zierikzee (ZZ) have been landfarmed since 1990. The experiments with sediments from the Petroleum Harbour (PH) and the harbour of Wemeldinge (WEM) were started in 1994. The experimental set-up of these landfarms has already been described in Chapter 4 and is summarised in Table 5.1. In the vegetated landfarms two layers are distinguished, an upper layer that was already dewatered and aerobic in the first year, and a lower layer for which several years were necessary to obtain an aerobic environment. During passive landfarming, vegetation has developed on all landfarms.

Table 5.1 Sediments investigated on Kreekraksluizen.

Type of sediment	Intensive landfarming	Passive landfarming	Number of layers sampled	Vegetation present since	Mineral oil concentration in original sediment (mg/kg d.m.)
PH, cultivated	1994 - 1996	1996 - present	1	1996	13,500
PH, vegetated		1994 - present	2	1995	13,500
WEM, cultivated	1994 -1 996	1996 - present	1	1996	2000
WEM, vegetated		1994 - present	2	1995	2000
GH	1990 - 1993[1]	1993 - present	1	1993	8100
ZZ	1990 - 1993[1]	1993 - present	1	1993	630

[1] Results published in De Groot and Van Lierop (1995)

Most of the research was conducted on the landfarm fields containing Petroleum Harbour and Wemeldinge sediments. During the whole degradation period, the landfarms were intensively sampled, as shown in Table 5.2. Period '0' was the original sediment. The high numbers of samples in the first years were taken, because a high degradation rate was expected.

Table 5.2 Number of samples taken for the analyses of mineral oil in the Petroleum Harbour and Wemeldinge landfarms.

	Period (year after start of landfarm)							
Type of sediment	0	0.5	1	2	3	4	5	7
PH vegetated upper	65	6	32	30	19	5	5	5
PH vegetated lower	65	6	16	15	17	5	5	5
PH cultivated	65	6	34	35	20	5	5	5
WM vegetated upper	19	13	21	30	19	5	5	5
WM vegetated lower	19	16	11	15	19	5	5	5
WM cultivated	19	17	21	30	19	5	5	5

The samples were analysed for mineral oil using NEN 5733 (GC-FID method, almost equivalent to ISO/DIS 16703). In this method 20 g of sample were extracted with a mixture of acetone and petroleum ether. The acetone was removed by extraction with water. According to this method, polar compounds that are not mineral oil were removed with florisil. In 1997 the amount of florisil specified in the NEN-method was increased to make the method also applicable for peat. The high amount of organic matter in peat implies a higher amount of co-extracted polar compounds. These have to be removed with a higher amount of florisil, which may lead to lower measured mineral oil contents. This change in the NEN-method has not been implemented to prevent a shift (extra decrease) in the measurement. Therefore, during the experimental period of the study, 3 g of florisil was used in each analysis. After concentration of the extract in Kuderna-Danish equipment, an aliquot was injected into a gas chromatograph with on-column injection and a FID-detector (Chrompack 9001) equipped with a CP7521 SimDis column (10 m * 0.32 mm df 0.1) and a CP 8008 retention gap (both supplied by Varian Chrompack). For quantification the area of the registered chromatogram between the retention times of the n-alkanes C_{10} and C_{40} has been integrated and compared with a standard prepared from the mineral oil standard supplied by RIVM, Bilthoven (RIVM-LOC01). This standard is prepared from equal amounts (mass) of Kuwait gasoil, purged to remove compounds smaller than C_{10}, and Shell Agip Basis Oil HVI 60. The chromatogram is given in Figure 5.1. All measured areas have been corrected for column bleeding.

The Geul Harbour and Zierikzee landfarms were analysed less intensively. From 1989 to 1993 samples were analysed using the Infrared method (IR) and published by De Groot and Van Lierop (1995). From 1995 the above described GC-FID-method was used.. Because the concentrations measured with these two methods differ, it was not possible to derive rate constants for the whole period.

The model to describe the degradation rate is the same as used for PAHs (Chapter 4) and is a sum of first order decreases (three-compartment model). The three compartments distinguished, are described as the fractions fast, slow and very slow degradable.

$$\frac{c_t}{c_0} = F_{fast} \cdot e^{-k_{fast} \cdot t} + F_{slow} \cdot e^{-k_{slow} \cdot t} + F_{veryslow} \cdot e^{-k_{very\,slow} \cdot t}$$

where:

c_t = concentration (mg/kg d.m.) at time t
c_0 = concentration (mg/kg d.m.) at time 0
F_{fast} = fast degrading fraction
F_{slow} = slow degrading fraction
$F_{very\,slow}$ = very slow degrading fraction
k_{fast} = rate constant fast degradation (y^{-1})
k_{slow} = rate constant slow degradation (y^{-1})
$k_{very\,slow}$ = rate constant very slow degradation (y^{-1})
t = time (year)

Plotting concentration (log-scale) against time, different consecutive linear parts can be distinguished if the rate constants differ enough in value, as has already been shown in Chapter 4. The different linear parts in the degradation curves have been fit with one single exponential function (Microsoft Excel). Because the size of the following degradable fractions does influence the values of the fitted parameters, the obtained rate constant values must be considered as actual values. The whole curve is not fitted with the above function, because the rate of dewatering influence on fast degradation and very slow degradation cannot always be recognised as already explained in Chapter 4. Both will influence the value of the rate constant for slow degradation.

5.3 Results and discussion

5.3.1 Composition of mineral oil in sediments

As already explained in Paragraph 5.1, original mineral oil products give a hump in a chromatogram, with individual separated n-alkanes on top. These n-alkanes are not visible in chromatograms of sediment (Figure 5.1). Not all oil components in the range C_{10} – C_{40} are present in the chromatogram from the sediments. Low boiling compounds ($<C_{14}$), which are easily degradable, are only present in low concentrations. After further degradation in the landfarm the hump remains, but is shifted to higher retention times, indicating that compounds in the range C_{10} till about C_{25} are most easily degraded. Slower degrading high boiling compounds are left. The original sediments and especially the Petroleum Harbour sediment contains many more low boiling compounds, compared to the sediment after 7 years of landfarming. Less then 20% of the residual oil in the remediated sediments consists of the fraction hydrocarbons in the C_{10}-C_{19} range, which pose the most risk (Brils *et al.*, 2002). Therefore, risks caused by mineral oil in sediment treated on a landfarm will be relatively small.

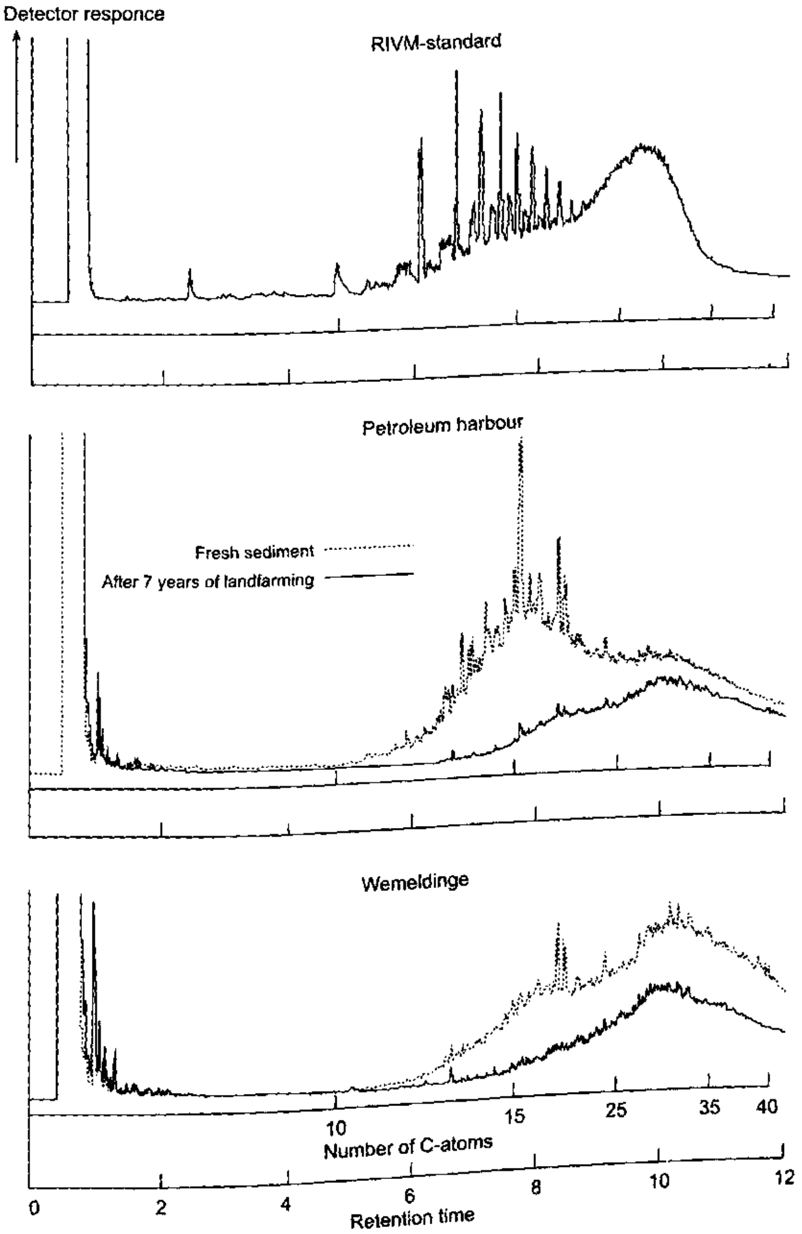

Figure 5.1 Chromatograms of mineral oil.

- Mixture of mineral oil as present in the RIVM standard.
- Mineral oil in the original dredged sediments from Petroleum Harbour and after 7 years landfarming.
- Mineral oil in the original dredged sediments from Wemeldinge and af-er 7 years landfarming.

5.3.2 Degradation of mineral oil

Mineral oil concentrations, obtained during 7 years of measurements in the vegetated Petroleum Harbour field, are presented in Figure 5.2 (upper figure). Measurement of mineral oil in sediment shows a large distribution of values, which can make it difficult to derive reliable degradation rates. Because of overlap, not all measured points are visible in this figure. In the original sediment the relative standard deviation of the measured mineral oil concentration was 37%, which was reduced to 15% after 5 years. The average standard deviation over the whole period was 24%. Relative standard deviations in the Wemeldinge sediment were slightly lower; decreasing from about 25% in the first years to 15 % after 5 years.

With so many data, the average value of the mineral oil concentration measured during a limited period is reliable. Values are averaged for half-year periods in the first year and for one year in the following period. The resulting values and fitted degradation curves are given in the second and third figure of Figure 5.2. Because of the amount of data presented in these figures, confidence intervals are not given, but they can be calculated using the relative standard deviation and the number of analysed samples given in Table 5.2. The 95% confidence values are about 10 % for the first 3 years and about 30% for the following years. This higher interval is the result of a limited number of measurements in these years.

In the upper layer of the vegetated fields and in the cultivated fields, fast degradable fractions were visible (first year of landfarming). The mineral oil concentration in the Petroleum Harbour sediment and Wemeldinge sediment were reduced by 55% and 50 % respectively in the first year, which means an actual degradation rate coefficient for the fast degradable fraction of 0.8 y^{-1} or higher (exponential decrease as a result of first order degradation). Taking into account the slow degradable fraction, the degradation coefficient for the fast degradable fraction becomes about. 3 y^{-1}. In Figures 5.2, the parts of the degradation curves representing fast degradation have not been fitted, because in this period the degradation rate is limited by the rate of oxygen introduction in the layer. A faster dewatering should have resulted in a higher rate constant. Under optimal conditions for degradation, Taylor and Viraraghaven (1999) reported a degradation coefficient for mineral oil of 9.8 y^{-1} (first order degradation). They remediated a clay soil contaminated with diesel fuel. If the soil or sediment is less suitable for landfarming, due to a low bioactivity, degradation rates can be smaller, as shown by Yerushalmi *et al.*, 2003. They found a degradation rate coefficient of 2.9 y^{-1}. The parts of the curves in Figure 5.2, after most of the fast degradable fraction have been degraded, and which represent slow degradation, have been fitted with an exponential curve. Very slow degradation was not observed.

The data of the lower layers of the cultivated fields of both sediments can be fitted with one single exponential curve. Dewatering and aeration in these lower layers took several years and oxygen was limiting (see also Chapter 7), which reduced the degradation rate of the fast available fraction. Fast and slow degradation could not be distinguished, and the fit is an overall fit in which the rate of dewatering and resulting degradation rates of the fast and slow degradable fractions are combined. These values cannot be compared with the values of the upper layers and the cultivated fields, because in the latter situations, degradation was not limited by oxygen. Comparable with the degradation of PAHs (Chapter 4), the degradation curve for mineral oil of the lower layer intersects the curve of the upper layer after approximately 7 years, which shows that the slow degradable fraction is responsible for the result after 7 years. Limiting conditions during the first years do not influence the results after 7 years.

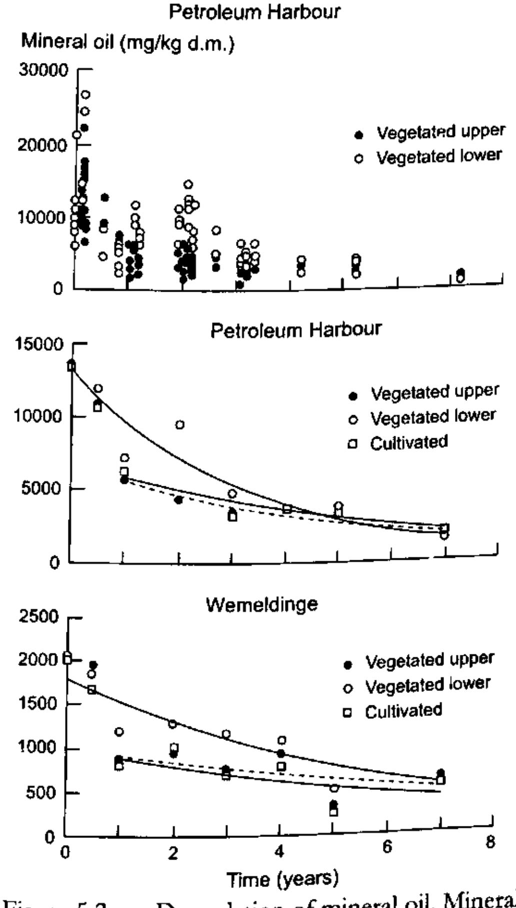

Figure 5.2 Degradation of mineral oil. Mineral oil concentration (C_{10} – C_{40}) as function of time.

- Vegetated Petroleum Harbour landfarm. Individual results are plotted.
- Petroleum Harbour landfarms, averaged values and fitted curves are plotted.
- Wemeldinge landfarms, averaged values and fitted curves are plotted.

Most important are the degradation rate constants of the slow degrading fraction in the upper layers of the vegetated fields and in the cultivated fields, starting after 1 year. This part of the degradation curves shows the slow degradation phase. The parameters of the fitted exponential curves are given in Table 5.3. The results of the Wemeldinge sediment are less accurate because of the large scattering of the measurements (lower correlation coefficient R^2). The values of the rate constants (k_{slow}) are presented as actual values, because the presence of a subsequent very slow degradable fraction is not considered. Values of k_{slow} are comparable for the different situations. The rate coefficients for the lower layers are larger, but in this fitm fast and slow degradation and dewatering are combined, giving k_{f+s} (assuming that the combined processes can still be considered as first order).

Table 5.3 Fitted parameters of first order degradation of the slow degradable fraction.(c_0= concentration at t=0; R= correlation coefficient).

	Period (y)	c_0 (mg/kg d.m.)	k_{slow} actual (y^{-1})	k_{f+s} (y^{-1})	R^2
PH vegetated upper	1-7	6384	0.172		0.91
PH cultivated	1-7	6884	0.169		0.87
WEM vegetated upper	1-7	1020	0.100		0.30
WEM cultivated	1-7	1033	0.131		0.32
PH vegetated lower	0-7	13052		0.299	0.93
WEM vegetated lower	0-7	1791		0.165	0.77

If no very slow degradable fraction is present, the slow degradable fraction will be the last fraction to degrade, and the actual degradation rate coefficient can be used to predict the end concentration or necessary treatment time. Presence of a very slow degradable fraction, however, will influence the rate constant for the slow degradable fraction obtained after fitting of the degradation curve. Estimating a value for the very slow degradable fraction, it is possible to refit the curves from Figure 5.2 and to obtain a real value instead of the actual value for the rate constant of the slow degradable fraction. In Figure 5.3 these results are presented for the Petroleum Harbour landfarms. Because the real value for the very slow degradable fraction is not known, the period of very slow degradation was not included in the measurements, and the real value of the degradation constant of the slow degradable fraction cannot be estimated. If the degradation curve is comparable with the one obtained by measuring the degradation of PAHs, the very slow degradable fraction will be the value after 7 years (see also Figure 4.8 in Chapter 4). In that case the degradation rate constant of the slow degradable fraction will be approximately 0.33 y^{-1}. If the degradation of mineral oil continues at the same rate after the first 7 years (first order degree), the very slow degradable fraction will be smaller, resulting in a value for the slow degradable fraction closer to the actual degradation rate constant.

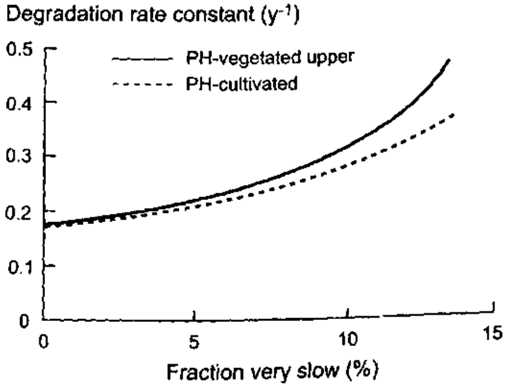

Figure 5.3 Effect of a very slow degradable fraction on the degradation rate constant of the slow degradable fraction. Petroleum Harbour landfarm, Vegetated upper layer and cultivated.

The actual degradation rate constants for slow degradation for PAHs (Chapter 4) and the actual rate constants for the degradation of mineral oil in Petroleum Harbour and Wemeldinge sediment are comparable. Therefore, the same constant can be used to predict degradation of both PAHs and mineral oil in other sediments. This does not mean that the time determining process for slow degradation is the same. Slow diffusion in soil aggregates will be the most important process for PAHs degradation and for degradation of mineral oil present at a low concentration. With the still high mineral oil contents after one year (6000 mg/kg d.m. in the Petroleum Harbour sediment), it is not expected that diffusion in soil aggregates will be limited. In Chapter 3 it has been shown that the mineral oil may associate strongly with the organic matter present in sediments. To degrade the oil it will therefore be necessary to degrade the organic matter or first to convert the organic matter to a form that releases mineral oil more quickly. Degradation rate coefficients of organic matter are of the same order of magnitude (see Table 2.5 in Chapter 2) as those measured for the slow degrading oil fraction. This aspect has not been investigated further.

The high mineral oil content in Petroleum Harbour sediment will probably be responsible for the large fast degrading fraction of PAHs in this sediment, as presented in Chapter 4. The mineral oil will act as a solvent for PAHs, and a large part of the PAHs will be present in the mineral oil phase. Diffusion of PAHs through this solvent to reach the pore water will be a rapid process.

The results of the older landfarm fields Geul Harbour and Zierikzee can be used to show if a very slow degradable fraction of mineral oil is present, as they did for PAHs. Results of the mineral oil determination in these sediments are summarised in Table 5.4. Because results of Infrared (IR)- and GC-FID-measurements may differ (Ouboter and Warbout, 1988), it is not possible to construct a degradation curve for the complete measurement period. Further it should be realised that using the GC-method, a background between 10 (sand) to about 150 (peat) mg/kg dm mineral oil can be measured when analysing sediments (Janssens and Groenewegen, 1997). At these levels, the method is less accurate.

Table 5.4 Mineral oil concentrations in the sediments from Geul Harbour and Zierikzee as dependent on treatment time. s.d. = standard deviation; n = number of analysed samples.

Years after start treatment	Geul Harbour				Zierikzee			
	Mineral oil (mg/kg d.m.)	s.d	n	Method	Mineral oil (mg/kg d.m.)	s.d	n	Method
0	8076[1]	34	2	IR	628[2]	206	3	IR
1	2308[1]	1020	5	IR				
2	1775[1]	866	4	IR				
4	493[1]	317	4	IR				
6	241	78	3	GC-FID	303	120	3	GC-FID
7	356	52	5	GC-FID	293	34	5	GC-FID
10	184	53	5	GC-FID	106	12	5	GC-FID
12	84	20	5	GC-FID	129	17	5	GC-FID

[1] De Groot and Van Lierop, 1995

[2] Average value reported by Serasea, 1991; TNO-Imet, 1991a and TNO-Imet 1991b

Geul Harbour sediment contained a large fast degradable fraction, as 75% of the mineral oil degrades within the first year (Table 5.4). In this Harbour, a tanker cleaning company was active before it was dredged. Probably the sediment was contaminated with mineral oil and surface-active compounds from this company (Frintrop, 2004 personal information). This may explain the high degradation in the first year. The original mineral oil concentration in the Zierikzee sediment was rather low, and the measured concentration after year 6 was already slightly above the limit of analysis. The mineral oil concentrations in both sediments were low in 2001; these sediments could be considered as clean in relation to this contaminant. Using the values measured with GC-FID (6-12 years), it is possible to derive a value for the rate coefficient for degradation in this period. The values for Geul Harbour and Zierikzee are respectively 0.20 and 0,18 y^{-1}. These values are comparable with the values for Petroleum Harbour and Wemeldinge in Table 5.3. R^2 values were respectively 0.78 and 0.80.

If these results are extrapolated to Petroleum Harbour and Wemeldinge Harbour sediment, it is to be expected that the slow degradation will continue and not stop after 7 years. This is in contradiction to the degradation of PAHs. Possible explanation is that the mechanism for oil degradation differs from the mechanism for PAH degradation. It is also possible that the very slow degradable fraction cannot be recognised due to the limitations of the measurement method involved. At a low mineral oil concentration (approx. 200 mg/kg d.m.), the limit of analysis of the GC-FID method for mineral oil makes recognition of a very slow available fraction impossible.

5.3.3 Prediction of the degradation curve

Comparable to the degradation of PAHs, the fast degradable fraction of mineral oil is degraded during dewatering. The slow and probably the very slow degrading mineral oil fractions are responsible for the degradation time necessary to reach the target value of mineral oil in sediments. Because a very slow degrading fraction was not included yet in the measurements for Petroleum Harbour sediment, the effect of this fraction is investigated using the three-compartment model. Petroleum Harbour sediment is the most heavily polluted sediment investigated (original mineral oil concentration 13,500 mg/kg d.m.), and the target value has not been reached within the 7 years of this investigation.

The effect of the presence of a very slow degrading fraction in Petroleum Harbour sediment has been plotted in Figure 5.4. A prediction, without a very slow degradable fraction, using the actual rate constant of Table 5.3, gives a mineral oil concentration below 500 mg/kg d.m. after 14 years of treatment. Longer treatment time to achieve the same result will be necessary if a very slow degrading fraction (12%) is included. Depending on the value of the rate coefficients for degradation of the very slow degradable fraction (0.08 or 0.03 y^{-1}), a treatment time between 16 and >40 years will be necessary to reach the target of 500 mg/kg.

The treatment time will be depend on the target value to be reached. The above used 500 mg/kg d.m. is based on the Dutch Building Material Act (Staatsblad, 1995), which makes it possible to reuse cleaned sediments and soil under restricted conditions. If higher target values can be used, the bioremediation time will be shorter. Using a target value for reuse of 1000 mg/kg, there may still be an influence of the very slow degrading fraction. A target value for reuse of 2000 mg/kg can be reached in 6-7 years of remediation for the heavily polluted sediment from the Petroleum Harbour.

Predicted treatment times of 7 years and 15-40 years are reasonable within the context of passive landfarming. However, long extrapolation times (>10-40 years) introduce new uncertainties. The soil developed from the sediment cannot be considered as a material with unchanging properties. The use of the soil developed from the sediments (as building material, arable soil, or soil in nature) may result in degradation of the original organic matter and also formation of new organic matter (residuals of vegetation that grows on the landfarm). As mentioned previously, the organic matter probably has an important role in the binding and degradation of mineral oil. The manner in which the soil is used use will influence the organic matter content and composition and may therefore influence the real degradation curve. Biodegradation will only continue in the next 40 years under aerobic conditions; the use of the soil during that time must ensure the presence of aerobic conditions.

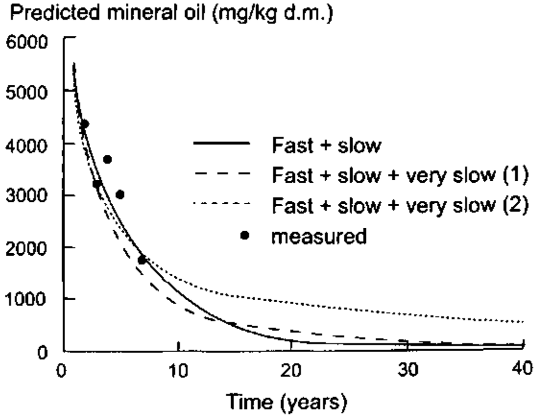

Figure 5.4 Calculted degradation curves and measured data in the upper layer of the vegetated Petoleum Harbour landfarm using the three-compartment model. Original concentration 13,500 mg/kg d.m. Distribution between avaialble fractions and degradation rate coefficients as follows:

Degradable fraction	Fast + slow		Fast + slow + very slow (1)		Fast+ slow + very slow (2)	
	fraction (%)	degradation constant (y^{-1})	fraction (%)	degradation constant (y^{-1})	fraction (%)	degradation constant (y^{-1})
Fast	55	3	55	3	55	3
Slow	45	0.17	33	0.3	33	0.3
Very slow	0	-	12	0.08	12	0.03

5.4 Conclusions

Mineral oil in sediment is not an easily degradable contaminant. This is the result of the way mineral oil is introduced into sediments. Mineral oil in sediment is a weathered oil and easily degradable compounds (low boiling compounds ($<C_{14}$) and n-alkanes) are not present or are only present in low concentrations. Comparable to the degradation of PAHs described in Chapter 4, a fast degradable fraction of mineral oil is present and can be degraded on the landfarm in one year, providing that aerobic conditions are obtained in the landfarm. The high mineral oil content in Petroleum Harbour sediment was likely responsible for the high fast degrading fraction of PAHs

in this sediment, as discussed in Chapter 4. The mineral oil will act as a solvent for PAHs, and diffusion of PAHs through this solvent to the pore water will be rapid.

The degradation of the following slow degradable fraction takes several years, and the degradation rate constants can be derived from the degradation curves. Over a period of 7 years, the degradation of the slow degradable fraction is responsible for the result of landfarming mineral oil polluted sediment. Using vegetation creates the necessary aerobic conditions quickly in the upper layer, but similar results are obtained in the slower aerated lower layer in a period of 7 years.

The actual rate coefficients for slow degradation of mineral oil and PAHs are of the same order of magnitude. The smaller importance of a very slow degradable fraction indicates that the mechanism responsible for degradation may be different. For PAHs diffusion in aggregates seems to be important. Probably the association of mineral oil with organic matter is important, and the turn-over of organic matter may influence the degradation rate.

The size of a very slow degradable fraction and its degradation rate constant could not be established in the Geul Harbour and Zierikzee sediment that have been treated for a longer period. This is in contrast to the presence of a very slow degradable fraction of PAHs in these sediments, as presented in Chapter 4. If a very slow available fraction of mineral oil is present in these sediments, it will be in the range of 0 – 200 mg/kg d.m., which could not be detected, because this is close to the limit of analyses of mineral oil in sediments.

The degradation rate is not the same for all compounds present in mineral oil. Easily degradable compounds are the first to disappear; therefore during landfarming the composition of the mineral oil in the treated sediment changes. Within the measured range C_{10}-C_{40}, the contribution of C_{10}-C_{19} to the measured concentration decreased during landfarming most rapidly. The range C_{10}-C_{19} is the range responsible for toxicity (Brils *et al.*, 2002) and therefore risks on a landfarm are reduced more quickly than the total concentration of mineral oil.

For three of the four investigated sediments, a target value of 500/mg/kg d.m. has been reached in a period of 5-7 years. For the heavily polluted sediment from the Petroleum Harbour (original concentration 13,500 mg/kg d.m.), this target value has not been reached, and more time will be necessary. How much time required will depend on the presence of a very slow degradable fraction.

Using the three compartment first order degradation model and a target value of 500 mg/kg d.m., treatment times from 15 years (fast and slow and no very slow degradable fractions) to more then 40 years (fast slow and very slow degradable fractions) can be predicted for the heavily polluted Petroleum Harbour sediment. For the other less contaminated sediments, 6 to 7 years are sufficient, providing oxygen is not a limiting factor. Using the target value of 500 mg/kg d.m., presence of a slow degradable fraction determines the required degradation time in these sediments. Intensivation of the treatment as described in Chapter 6 has limited effect on this rate.

Therefore, long treatment times (6 years or more) are necessary, and passive landfarming (which reduces input of labour and energy as much as possible, see Chapter 1) is recommended for landfarming of mineral oil contaminated sediment. Using the higher target values of 2000 mg/kg d.m. introduced in 2004 changes this conclusion, because in that case removal of the fast available fraction may be sufficient for many mineral oil polluted sediments. Lower target values will make longer treatments necessary.

Test for prediction of the degradation of the fast degradable fraction of PAHs have been shown to be possible (see Chapter 3 and 4). However, it was not possible to correlate results of these tests to mineral oil, with the degradation rates observed on the landfarms. During development of the tests for PAHs, knowledge on the mechanisms responsible for the degradation rate was obtained. Development of tests to predict the degradation of mineral oil may have the same function and give a better understanding of mechanisms involved in biodegradation of mineral oil. It will, however, be difficult to develop such a test because of the differences in mineral oil properties (i.e., physical, boiling point, degradability, and polarity).

6 Effects of optimisation of landfarm treatment of sediments on bioremediation

6.1 Introduction

6.1.1 Optimisation on a landfarm

Landfarming is an inexpensive, but relatively slow bioremediation process for degradation of organic contaminants in sediment and soils. It is part of human nature to improve and to optimise landfarming systems that are in use, with respect to biodegradation rate and biodegradation efficiency. Landfarming, especially passive landfarming as applied on Kreekraksluizen, is one of the cheapest bioremediation methods. Optimisation may increase costs in most cases and optimisation should therefore lead to improved results; lower residual concentration in a shorter time. If this can be shown, then the use of the optimised method can be considered, even if not associated with passive landfarming. Otherwise passive landfarming will be the proper choice.

In this chapter the possibilities of optimisation on a landfarm are discussed. The process of bioremediation can be optimised by improving the activity of degrading organisms and the mass transfer processes in the sediment. The most optimum system regarding biodegradation rate and biodegradation efficiency is a bioreactor-like system, in which slurry is treated at optimum temperature, is mixed and in which oxygen, nutrients and eventually surface-active compounds to increase chemical solubility are added. As shown in Chapter 2.2.2, a slurry reactor is the most optimum system for mass transfer because the high water content in a slurry increases the desorption rate. A discussion of the bioreactor system is beyond the scope of this thesis as this study is limited to addressing landfarm systems. A landfarm is characterised by water that is present in unsaturated conditions in which oxygen is supplied by diffusion through gas filled pores in the landfarm medium. Lack of mixing limits the possibilities to increase the biodegradation rate in a landfarm.

"What is possible under landfarm conditions?" should be the first question to answer. Increasing the moisture content to increase the mass transfer, without active introduction of oxygen will lead to an anaerobic sediment in which no degradation will occur. If working under water saturated conditions was effective, then it should also be easy to do this in-situ and clean the sediment in its own water system. These technologies do not work (Ferdinandy, 1999) or may be expensive, because an active electron acceptor has to be included (Mysona and Hughes, 1999). The fraction easily degradable organic matter present in sediment (see Chapter 4.3.3) will be responsible for a high demand of the electron acceptor. In this chapter technologies are discussed to increase the remediation rate on a landfarm. Landfarming of sediments has three partly overlapping phases:

- Dewatering and ripening of the sediment, so that the sediment becomes aerobic and degradation is initiated.
- Fast degradation of bioavailable contaminants.
- Slow and very slow degradation of contaminants well adsorbed in the soil matrix.

Every phase can be accelerated to shorten the overall treatment time. The time necessary for dewatering and ripening of dredged sediment can be shortened by tillage. Vegetation also stimulates dewatering and ripening by a more intense evaporation. The subsequent biodegradation may be stimulated by forced aeration, higher temperature, addition of substrates and nutrients, and activation of soil life. The following ways of optimisation have been studied which can be effective on a landfarm:

- Dewatering of the sediment using tillage and vegetation.
- Use off elevated temperature and forced aeration in the dewatered sediment.
- Adding degrading organisms in the form of fungi.
- Use of vegetation including nutrients to activate microbiological soil activity.

Results of these optimisations have been compared with the observed degradation on the ongoing landfarm experiment on the landfarm Kreekraksluizen as described in Chapter 4 and 5. The measured bioavailability will be used to explain the results. Published results of bioreactors with the original sediments used in this chapter (Ferdinandy, 1997; Stefess, 1997) are also included in this evaluation.

It is not the intension of this chapter to exhaustively discuss the optimization methods used, as this would require several more chapters. Not only the possibility of applying the methods, but also the effect on bioremediation compared to the results on the landfarm Kreekraksluizen, are considered. If improved bioremediation can be shown, resulting in a higher degradation rate combined with lower residual concentration, a further optimization study is justified to improve results and reduce the costs.

6.1.2 Dewatering

Oxygen, which is necessary for biodegradation, can be introduced in dredged sediment by replacing part of the water filled pores by air filled pores. Part of the water has to be removed in order to create aerated sediment. Dewatering or lowering of the water content is possible by removing the excess of water through drainage or evaporation. As long sediment remains over saturated with water, a good drainage system is needed. After a certain time for drainage, the sediment will act like a sponge and retain the remaining water. After this time the water content can be lowered using under- or over pressures, like in filter presses, and by stimulation of evaporation. The option of over pressure, however, is not an option in a large-scale landfarm system.

Parallel with the investigation on Kreekraksluizen, it has been investigated if the dewatering of the Petroleum Harbour sediment could be improved in a hall-system (enclosure and management) as present near the Petroleum Harbour (Ferdinandy, 1999). Advantages of a hall are the higher temperature and better control of humid content by elimination of rainfall. In an open landfarm, not only the water present in the sediment has to be removed, but also the precipitation. While on first sight the hall was an attractive procedure, in practise however it did not work. In the hall, the air was almost 100% saturated with water, which reduced the evaporation. The water could only be removed by forced ventilation. From an energetic point of view this is not attractive. Energy saving measures are possible to apply, but this will also increase the investment costs.

In outside systems ventilation is not a problem and evaporation from the surface will occur even under colder winter conditions. The extra precipitation can be prevented by construction of a simple roof system under which the wind can still blow or through use of porous films. This will decrease the time necessary for dewatering, but will finally end in a very dry system in which biodegradation will stagnate by lack of water. Sprinkling of the dewatered sediment will prevent this.

In an open landfarm system it is only possible to increase the surface evaporation by renewing the surface (tillage) or using vegetation. If fully covered vegetation is present, then the evaporation is at maximum. It is necessary to take measures to remove the rainfall. Under Dutch conditions, there is more rainfall (800 mm) then evaporation (600) mm. Fortunately, in summer evaporation exceeds the rainfall (Figure 6.1). Removal of the excess rainfall can be based on techniques developed in the polders in The Netherlands (De Glopper, 1985).

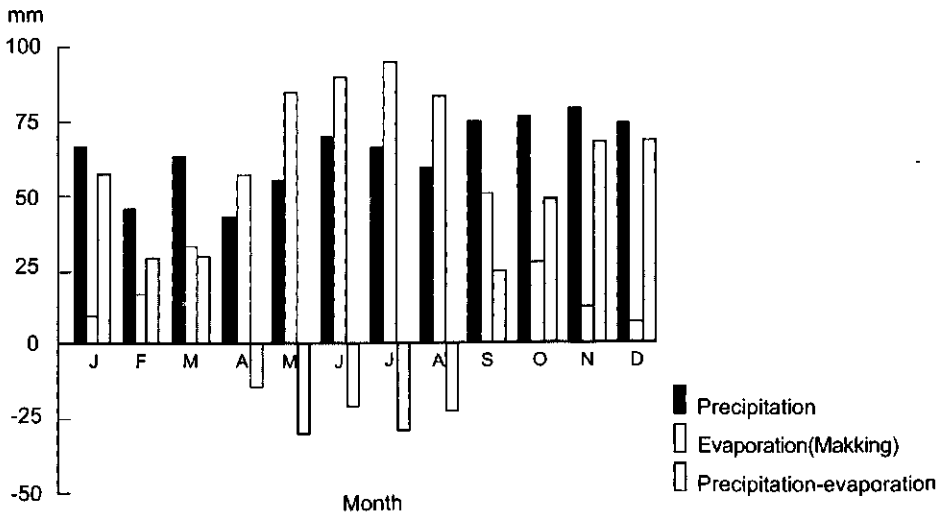

Figure 6.1 Precipitation and evaporation in an 'average' Dutch year (KNMI, 2004).

The optimisation of dewatering is described using two simple ways of increasing the evaporation, both in combination with the removal of the excess of rain. They are studied on the landfarm Kreekraksluizen.

- Tillage and cultivation creates new surfaces from which evaporation continues. Without tillage the dry surface crush will act as an isolator and preventing further evaporation.
- Stimulation of vegetation to create a well-rooted vegetation over the whole surface of the landfarm. The evaporation from a vegetated surface is much higher than from a bare surface.

Application of an underpressure to increase the amount of drained water has also been investigated.

6.1.3 Forced aeration and higher temperature

Landfarming terrestrial soil can be improved by forced aeration. This is applied on biopiles (Von Fahnenstock, 1998) and by application of landfarming under covered conditions like hall farming (Freijer, 1994; Riedstra *et al.*, 1997). In fresh sediment forced aeration is only possible in a bioreactor. A biopile or hall farming system for sediments can only be applied after dewatering of the sediment, because it is necessary that a stabile structured material is applied in those systems, to assure enough air filled pores.

Application of elevated temperature in combination with forced aeration in an outside landfarm is not energetically effective, because high losses of energy can be expected. This will only be possible on sites where residual heat is available like on an industrial plant. Steketee and Huisman (2000) have investigated the possibility to start a landfarm for sediment near an energy plant and to use the excess of heat. Their study was focussed on the effect on dewatering and according to their results, acceleration of ripening with a factor 2 seems possible. The heat demand was very high and their procedure will only be effective if energy is freely available. The model results in Chapter 2.5 showed that a higher temperature did not have a positive effect on aeration. Although the activity of organisms is higher at higher temperature, the degradation of organic matter necessary for ripening does not occur sufficiently, because the supply of oxygen is limited. Cultivation gives also an acceleration of ripening with at least factor 2. This is showed not only using the model (Chapter 2), but also experimentally by intensivation of the cultivation of the sediment as described further. Application of heat, starting with fresh sediment, is not further investigated in this study.

As shown in the previous chapters, the fast degrading fractions of PAHs and mineral oil are degraded during the dewatering process. Forced aeration and elevated temperature should therefore be effective for the slow and very slow degradable fraction.

6.1.4 Adding of substrate containing active fungi

White-rot fungi have the ability to metabolize contaminants by their production of extracellular ligninolytic enzymes (Bar and Aust, 1994). *Phanerochaete chrysosperium* (Hammel, *et al.*, 1986) and *Bjerkandera sp. BOS55* (Kotterman *et al.*, 1998) are well known for degradation of contaminants. Use of fungi in biofilters to degrade volatile aromatic hydrocarbons is suggested by Prenafetta Boldú (2002). The commercial available fungi *Pleurotus spp.* (oyster mushroom) has been used to increase the biodegradation rate of PAHs in a soil from a former manufactured gas plant site (Bogan and Lamar, 1999) and creosote contaminated soil (Eggen *et al.*, 1999). Based on laboratory research, the degradation of PAHs by fungi has been promoted for full field application (van der Meene, 1994; Field *et al.*, 1995). However, full-scale remediation of a PAH contaminated vadose zone soil that could not be accomplished with native microorganisms but was accomplished by augmentation using the white rot fungi has not been demonstrated.

Most fungi grow on substrate. For further growth and survival it is necessary to inoculate them and add them to the sediment together with the substrate. The production of an active substrate makes the use of fungi expensive. In view of the major importance attached to the economical feasibility of the method, commercially grown residual fungal substrates from *Agaricus bisporus* and *Pleurotus spp.* are favourable, which are substrates produced in large amount in order to grow mushrooms. The major mushroom production countries are the USA, France, the Netherlands, England and Italy. In 1993, 190 million kg of mushrooms was produced in the Netherlands (Van Horen, 1994). This gives finally a large amount of residual substrate, 5 kg for every kg of mushrooms. The fungi in the residual substrate are still active and the substrate is available for free and could be used to stimulate biodegradation, providing no residual pesticides are present. *Agaricus bisporus* and *Pleurotus spp.* also produce extracellular ligninolytic enzymes although they are less active compared to *Phanerochaete chrysosperium* and *Bjerkandera sp. BOS55* as shown in Table 6.1 (Nobis, 1998).

Table 6.1 Production possibilities of extracellular oxidative enzymes.

	Ligninolytic enzymes					
Fungi	Lignine peroxidase	Mn peroxidase	Peroxidase	Lactase	Glyoxal oxidase	Aryl-alcohol oxidase
Agaricus bisporus	(+)	+		+		
Pleurotus spp.		+		+		+
Phanerochaete chrysosperium	+	+			+	
Bjerkandera sp. BOS55	+	+	+	+	+	+

De Jong *et al.*,1994, values for *Agaricus bisporus* Bonnen *et al.*, 1994

The endogenous microbiological population developed during dewatering of sediments is able to degrade the fast degradation available fraction of PAHs and mineral oil (see Chapter 4 and 5). Fungi are reported to be able to degrade PAHs and are not applied for mineral oil. Added fungi must have a function in the degradation of the slow and very slow degradable PAHs. Sediments are not aerobic from origin; they are completely saturated with water. Because fungi cannot survive under these conditions, it is necessary to dewater the sediment. Figure 6.2 gives the period of time in which adding of fungi may have a positive effect on the degradation. In this period the endogenous population has already degraded the PAHs available for fast degradation. Slow and very slowly degradable PAHs are still present.

To be successful, addition of substrate with active fungi after dewatering of the sediment must lead to a lower residual concentration compared to the residual concentration obtained on a landfarm without addition of fungi (compare line Sediment + substrate + active fungi and line Sediment in Figure 6.2) . Substrate in which fungi are supplied also contains nutrients and organic matter and the substrate may also have a positive effect on degradation. To distinguish the effect of fungi from the effect of substrate, the addition of deactivated substrate (fungi are killed) instead of substrate with living (active) fungi is also investigated. (Line sediment + deactivated substrate in Figure 6.2).

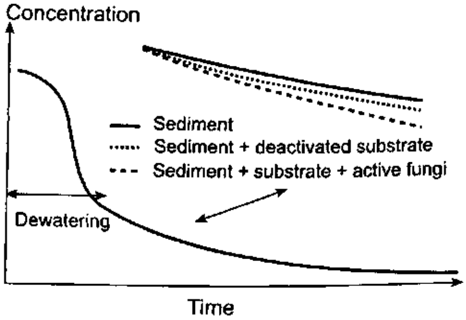

Figure 6.2 Hypothesis of the effect of adding of substrate with and without active fungi during bioremediation of PAHs contaminated sediment.

6.1.5 Activation of microbiological activity in soil by vegetation

Vegetation may have a stimulating effect on biodegradation. Use of vegetation also called phytoremediation or more specific phytodegradation (Japenga, 1999) has been used for the removal of organic pollutants (April and Sims, 1990; Cunningham *et al.*, 1996). Several factors may be of influence:

- Root activity stimulates the ripening of the sediment, giving an improved soil-structure.
- Roots are able to penetrate small soil aggregates, which reduces the average aggregate size further. Desorption from small aggregates is faster (see Chapter 2.2.2).
- By reducing the aggregate size, the surface (especially for mineral oil) to be attacked by micro-organisms increases.
- Root exudates increase the amount of dissolved organic carbon, which may have an effect on the diffusion rate (see Chapter 2.2.1) and thereby on the degradation rate.
- Soil roots stimulate the microbiological life in soil, which also may have an influence on the degradation rate. Associations between plant roots and fungi (arbuscular mycorhizas) have an important role in the degradation process (Joner *et al.*, 2001). Roots release compounds that selectivily foster contaminant degrading micro-organisms (Fletcher *et al.*, 1995). Root turnover produces compounds that stimulate the growth of bacteria that can also degrade contaminants (Leigh *et al.*, 2002).

Phytoremediation is not a proper method if the decrease of PAHs or mineral oil contents is the result of uptake by the vegetation. This will lead to high risks for organisms consuming the vegetation. However, uptake by vegetation is not to be expected because of the high octanol/water partition coefficient (K_{ow}) of the non-polar compounds involved (Sims and Overcash, 1983). In sediment, this value is not only high for PAHs but also for mineral oil, because more polar compounds are not present in sediments. If PAHs are present in harvested plants their origin is deposition from air or splashed soil particles and not the result of root uptake. (Anderotti *et al.*, 2001; Delchen *et al.*, 1999; Samsøe-Petersen *et al.*, 2002, Japenga *et al.*, 2003). Uptake of volatile mineral oil components is possible (Briggs *et al.*, 1983; Burken, 2001), but these compounds are not present in sediments.

6.2 Materials and methods

6.2.1 Origin of the sediments and applied optimisation methods

The optimisation studies have been done with Petroleum Harbour and Wemeldinge sediment from the landfarm Kreekraksluizen. This landfarm and sediments have already been described in Chapter 4.

Evaporation, which is necessary for dewatering, was stimulated by tillage, or by using natural vegetation (1994 and following years). In a separate container the effect of underpressure on dewatering was tested (1994). After dewatering, the sediments were treated and monitored as described in Chapter 4 and 5. In portions of the fresh or partly remediated sediment bioremediation has been stimulated using;

- Degradation under optimum landfarm conditions; higher temperature and extra addition of oxygen (1995).
- Introduction of substrate containing active fungi (1997 and 1998).
- Optimization of plant growth and stimulation of microbiological soil activity (1999).

The efficiency of stimulation has to be compared with a reference situation. The original anaerobic sediment cannot be used for this purpose, because no degradation will occur in the original anaerobic sediment. The experiments were conducted in order to improve the results of landfarming and, therefore the effectiveness of the different stimulations is compared with the results of the long-term treatment study described in Chapter 4 and 5. During this study, parts of the treated sediment have been used for the different optimisation studies.

6.2.2 Dewatering

Dewatering has been stimulated using tillage and natural vegetation. Due to problems that were related to constraints with regard to Dutch legislation, cultivation in the first year could not be optimised and another year was necessary. The reason for these problems was the concentrations of the contaminants in the Petroleum Harbour sediment. They were above the maximum allowed concentration on the landfarm site and during the first summer period activities were legally forbidden. In the second year a ditch was implemented in the middle of the landfarm and the water in this ditch was constantly removed using a pump (see Figure 4.2 in Chapter 4). The water from the ditch and the drainage system below the sediment was collected and could be discharged to the surface water (see also Chapter 7). Besides the ditch to stimulate dewatering, the sediment was cultivated (tillage) in half of the fields to increase evaporation of water. Tillage started with the dried top layer together with part of the wet sediment until the drainage layer was reached. In the other fields vegetation was allowed to grow also in order to stimulate evaporation. Because of the salt origin of Wemeldinge sediment and brackish origin of Petroleum Harbour, salt tolerant reed was planted in the first year. Natural vegetation was allowed to grow. Dewatering by the drainage system was measured due to measurement of the discharge of water by this system. The effect of dewatering (aeration) was visually observed:

- Black; the sediment is anaerobic.
- Brown, the sediment is aerobic.
- Brown with black, the sediment is partly aerobic.

The effect of creating an extra underpressure has been tested in containers of 6 * 2.3 * 2.5 m (length*width*height) with a sediment layer of 1.6 m and a drainage layer of 60 cm. The container had been divided in two compartments. One compartment could be naturally drained and the other one had an underpressure of 50 cm water. Water tension had been measured using water filled tensiometers. The experiment had been started half of September 1994. On October 13, 1994 the containers have been covered with sail cloth to prevent the large amount of autumn rain to enter the sediment.

6.2.3 Forced aeration and higher temperature

Landfarming under optimal conditions have been carried out with portions of dewatered sediment in 1995. The sediments were dewatered and the fast degradable fraction has been degraded. Sediments from the cultivated landfarms have been used. Originally it was planned to do the research in commercial bio-units in Vlagheide. Due to time necessary to fulfil all legislations this was not possible and the process has been simulated in Rosmalen at the Heymans Company were all permissions were present. Containers of 6 * 2.3 * 2.5 m (length*width*height) have been used, which were provided with a drainage layer of 50 cm containing tubes (10 cm drainpipes) for the supply of air (Figure 6.3). Heating tubes were present on top of the drainage layer. A sediment layer of 120 cm has been used. The dewatered sediments have been taken from the landfarm on Kreekraksluizen on July 7, 1995 and sieved before filling to decrease the aggregate size and improve the structure on a sieve of 15 * 15 cm. The sediments have been sampled on Kreekraksluizen and the transport has been considered as part of the intensivation process. The sediments were already structured although the centres of larger aggregate were still anaerobic. The moisture contents of the used Petroleum Harbour and Wemeldinge sediment were respectively 30.3% and 21.7%. In the sediment layer cells for measuring oxygen and temperature have been installed. The whole systems were covered to prevent cooling and rainfall on the sediment.

Unfortunately there was a gas explosion in the heating devise directly after start of the experiment (July 13, 1995). The authorities have investigated this and the real experiment with forced aeration started after 49 days (August 24, 1995). Before starting the forced aeration, the sediments were sieved again, because the structure of the sediment deteriorated. A start date of the experiment of July 7, 1995 has been used, because temperature in the period between July 13, 1995 and August 24, 1995 has been relatively high (summer period). On October 10, 1995 the sediments have been sieved another time (see also results) and the thermostatic system has been optimised because the sediments in the containers were cooled down to much by the lower outside temperature.

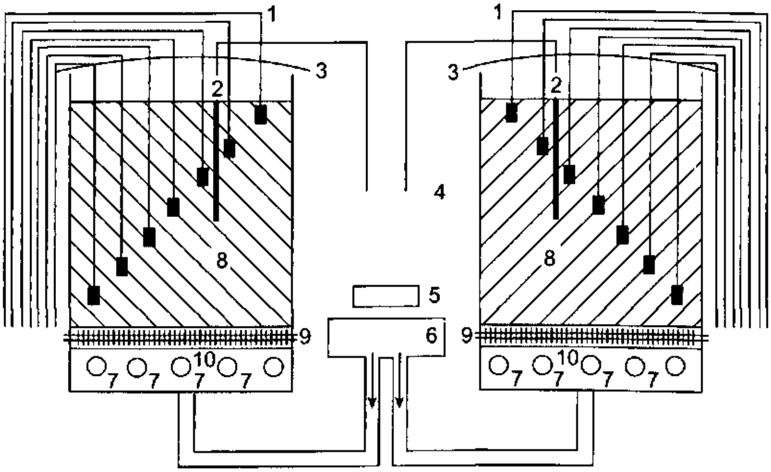

Figure 6.3 Schematic presentation of the aeration and temperature experiment. 1 Oxygen cells, 2 Temperature sensor; 3 Cover of the containers, 4 Heating devise, 5 Thermostat, 6 Blower, 7 Tubes for air supply; 8 Sediment, 9 Heating tubes, 10 Drain sand.

During the experiment of total 154 days samples have been taken to measure PAHs and mineral oil as described in Chapter 4 and 5. Temperature and oxygen have been measured.

6.2.4 Adding of substrate containing active fungi

The experiments with fungi were designed to be applicable for future field application and not to find the optimum amount of fungi. Mixing of the sediment should be easy and not leading to an unacceptable dilution. Therefore, the mixing ratio was 1:1 on the basis of volume; 28% and 20% (on weight) for respectively *Agaricus bisporus* and *Pleurotus spp.*. The hypothesis described in 6.1.4 and illustrated in Figure 6.2 has been tested on three levels:

- *Controlled system in containers on a research laboratory.* These systems on the Mushroom Experimental Station in Horst were designed to produce mushroom substrate. The containers were placed in a tunnel during 24 days and temperature and aeration were controlled. The size of each container was 105*105*180 cm (length*width*height). They were filled with 100 cm sediment or sediment substrate mixture. The following experimental set up has been used:
  - Sediment only, the sediment was not mixed with a substrate but received a treatment, comparable to the sediments in the other containers (blank).
  - Sediment mixed with substrate, *Agaricus bisporus* or *Pleurotus spp.*
  - Sediment mixed with deactivated substrate (no active fungi). This was achieved by steaming the substrate during 12 h. at 70 °C.
- *Test system in a soil-cleaning hall (Bion).* The soil cleaning hall of the company Bion in Almelo (The Netherlands) was used for this part of the experiment. Conditions in the hall were simulated in small containers during four months. It was possible to aerate and to irrigate the soil (Riedstra *et al.*, 1997). Experiments had the same design as in the containers. An extra blank has been used in which the nutrient mixture normally applied in the hall has been added (further mentioned as Bion blank).
- *Outside experiment on a landfarm.* The outside landfarm was situated near the Kreekraksluizen in the southwest part of the Netherlands. On this site several sediments have been treated by landfarming. On this site only the *Agaricus bisporus* has been tested in different layer thicknesses, 30, 50 and 100 cm during 4 months. Again necessary blanks have been used.

Dewatered and ripened sediment from the Petroleum Harbour was used. The PAHs (Dutch National List) and mineral oil (C_{10}-C_{40}) concentrations in this sediment were original 550 and 13,500 mg/kg d.m. The sediment taken for this experiment had already been dewatered and landfarmed during 2 years and the residual concentrations were approximately30 mg/kg d.m. for the PAHs and 4000 mg/kg d.m. for mineral oil. In the Bion hall also fresh sediment from the Water Council 'De Drie Ambachten' and a soil from a former manufactured gas plant (Stadskanaal) was tested.

Although fungi were not expected to have effect on the mineral oil concentration, mineral oil in the treated sediments was analysed. PAHs and mineral oil have been measured as described in Chapter 4 and 5. Results have been corrected for the added amount of substrate.

6.2.5 Activation of microbiological activity in soil by vegetation

In 1999 sediments of the lower layer of the vegetated landfarms was sampled and with these sediments, pots (two series of 18 pots) were filled (approx. 8 kg/pot). Three levels of nutrients were applied in order to optimise plant growth (0 = no nutrients; M = medium and H = high). Amounts used were respectively 0; 288 and 575 mg KCl/pot, 0; 897 and 1795 mg triplesuperphophate/pot and 0; 255 and 510 mg neutral nitrogen fertilizer (27% N)/pot. The pots were sewn with grass (*Agrostis capillaris*) or Lucerne (*Medicago sativa*). Blanks without vegetation were installed with 0- and M-level of nutrients. The pots with Lucerne did not receive nitrogen, because this vegetation is a nitrogen fixator.

To one treatment with medium level of nutrients and no vegetation extra organic substrate (glucose+ glycine in an amount equivalent to 3000 kg/ha) has been added in small portions during the experiment. This was done to discriminate between physical effects of the roots and the effects of root exudates. The organic substrate had to mimic as an extra amount of exudates. The experiment had last 2.5 months and the pots were placed in a glasshouse to remain optimum conditions for grow of vegetation. The crop-production was measured. The content of mineral oil and PAHs and the availability of PAHs using the Tenax -method were measured at the end of the experiment (2.5 months). The measured concentrations were compared with the concentration measured on the landfarm at Kreekraksluizen at that moment.

After 2.5 months the pots were stored under the same conditions in the glass house. Vegetation was stimulated and the sediment was sampled another time in October 2003 (after 4 years) and analysed on PAHs.

6.2.6 Measurement of the fraction available for fast degradation

A chemical-measured value for availability of PAHs can be obtained using the Tenax-method described by Cornelissen *et al.* (1997). This method has already been described in Chapter 3. As explained in Chapter 5, no method was available for predicting the fraction of mineral oil available for fast degradation.

6.3 Results and discussion

6.3.1 Optimisation of landfarming versus passive landfarming

Several optimisation experiments have been carried out in this study. As mentioned before, each experiment could be a study on its own, which was not the aim. In this chapter, the results of experiments applicable on a landfarm are described briefly and more attention is paid to the comparison of all results, especially the effect of optimisation compared to the treatment on the passive landfarm. The results of the different experiments are described and discussed in the following sections. The same order has been used as described in the material and methods section. An overall evaluation is described in following Section 6.4.

6.3.2 Effect of dewatering

As described before, it was not allowed to handle the sediment in the first summer. Summer 1994 was a very hot summer, resulting in a quick drying of the top layer of the sediment. At first transfer of moisture to the top layer took place by capillary action. After a week however capillaries were broken and a dry crust had been formed (visual observation), preventing optimum evaporation (evaporation reduction). Due to compaction (see Chapter 2.4.2) the volume reduced and excess of water had been discharged by the drainage system. The discharge rate of drainage water, however, was very low (Figure 6.4). Drainage from the Petroleum Harbour fields started after a week. In the Wemeldinge field drainage started immediately, but reduced strongly after a week, following the Petroleum Harbour curve till the end of the measuring period. Discharge of drainage water in both sediments stabilised around 0.2 m^3 per day, which is equivalent with 0.7 mm/d. Precipitation in this period was 1 mm/day. After the measuring period the rainfall increased and potential evaporation decreased (beginning of autumn) resulting in fields that were fully covered with water. The discharge of drainage water increased to 1 mm/day (0.3 m^3/d). The low amounts of drainage water, in spite of the wet conditions of the sediments, indicate a low permeability of the sediments for water.

With vegetation, the same result (aerobic soil) was achieved with a delay of about two years in the Petroleum Harbour sediment and three years in the Wemeldinge sediment. The Wemeldinge field needed more years to become aerobic which can be explained by the higher salt content that had a negative effect on the development of vegetation.

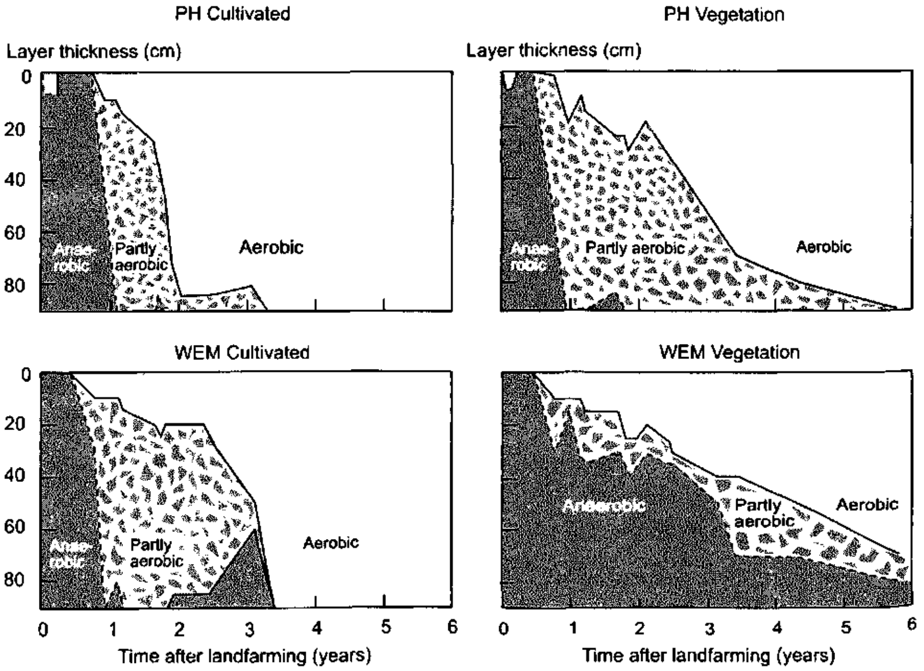

Figure 6.5 Partitioning of the aerobic, partly aerobic and anaerobic layers in the Petroleum Harbour (upper figures) and Wemeldinge fields (lower figures).

6.3.3 Effect of forced aeration and higher temperature

Oxygen supply is essential for biodegradation. In the Petroleum Harbour sediment the oxygen concentration in the pore gas as measured in the containers was 21% (volume) during the whole period. This does not mean that the oxygen supply was optimal for the whole sediment. Until the last sieving of the Petroleum Harbour sediment treated in the container on day 95, aggregates were recognised which were black (anaerobic) in the centre especially in the lower part of the container. The oxygen concentration in pores in the Wemeldinge sediment was approximately 10% in the first 95 days. Sieving the sediment and refilling the container on day 95, improved the aeration and an oxygen concentration of 21% was measured till the end of the experiment. Visually the structure of the sediment declined again during this lasts part and black anaerobic parts became visible. With a longer treatment in the container another sieving should have been necessary to improve the structure. This shows that in an optimised system structure stability is also an important factor.

The concentration of PAHs and mineral oil is presented in Figure 6.6. It is clear that in the Petroleum Harbour sediment both contaminants are further degraded. These concentrations were also relatively high. In Wemeldinge sediment a further degradation of PAHs is not visible and a slight degradation of mineral oil is observed.

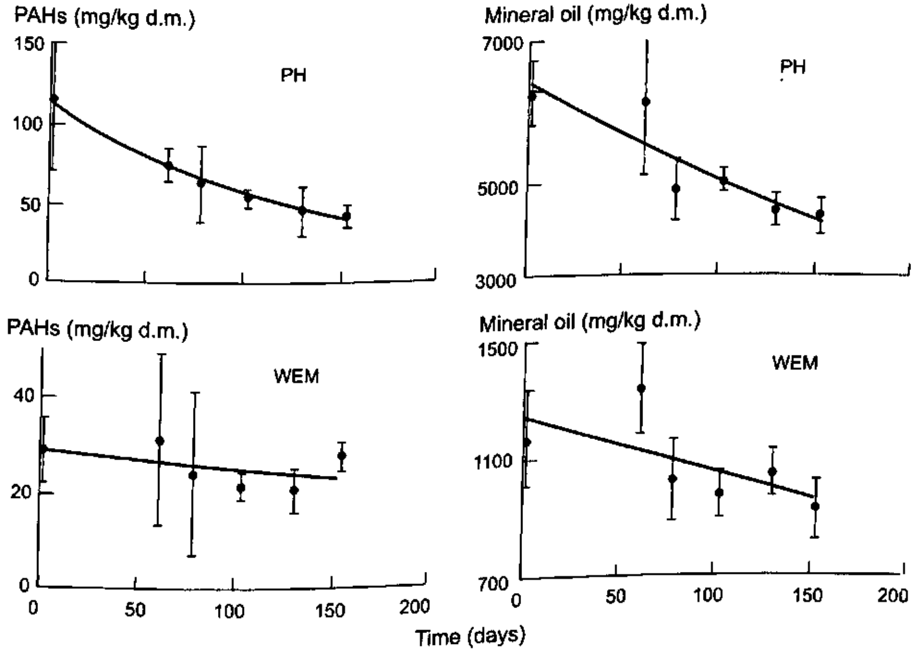

Figure 6.6 Degradation of PAHs (Dutch National List) and mineral oil in the experiment with forced aeration and high temperature, including 95% confidence values. Petroleum Harbour (upper figures) and Wemeldinge fields (lower figures).

Using the values of Chapter 4, approximately 50 mg/kg d.m. PAHs present in the used Petroleum Harbour sediment is slow or very slow biodegradable, which means that the sediment in the container experiments contained about 60 mg/kg d.m. fast degradable PAHs. Most of the original fast degradable PAHs in the sediment had already been degraded before starting the optimisation experiment. The fast degradable fraction in the used Wemeldinge sediment will be very small, because the PAHs-concentration has already the level of the concentration observed in the landfarm in year 2 and 3. The observed decrease of the PAHs in this sediment is low and in agreement with the low fast degradable fraction.

Using the data for mineral oil presented in Chapter 5, the used Petroleum Harbour sediment contained about 1000 mg/kg d.m. fast degradable mineral oil and 4000 mg/kg d.m. degradable during 7 years of landfarming In the Wemeldinge sediment these values are respectively 400 and 300 mg/kg d.m. In Wemeldinge sediment only the fast degradable fraction has been removed during the 150 days of the intensivated treatment. In the Petroleum Harbour sediment more than the fast degradable amount was degraded in this period. The concentration in this sediment is much higher and oil will be present as a separate phase (see also Chapter 5). Intensivation of the treatment will lead to increase of the oil surface, which is available to be attacked by degrading organisms.

The PAHs and mineral oil in the sediment are not volatile and will be bound by the sediment. Volatilization was not expected and was not observed using organoleptic observations. Volatilization, however, was not measured. If forced aeration will be applied, then the risk of volatilization and emission to the air can be limited by using a filter system as often applied in hall systems.

The data in Figure 6.6 have been fitted with an exponential curve (like in Chapter 5 and 6) and the actual degradation rate constants and the correlation coefficients (R^2) s are given in Table 6.2. In this table, the fitted values are compared with the values of the degradation rate coefficients obtained in Chapter 4 and 5. The actual rate constants for the degradation of PAHs and mineral oil in Petroleum Harbour sediment are close to the value for fast degradation reported in Chapter 4 and 5. As mentioned before, there was still fast degradable contaminant present in the treated sediment. In the Wemeldinge sediment the rate coefficients for degradation are between the values for slow and fast degradation as found for the landfarm Kreekraksluizen.

Table 6.2 Actual rate coefficients (k) for degradation of PAHs and mineral oil in the forced aeration experiment. Values are compared with the actual degradation rate coefficients obtained in Chapters 4 and 5. k-values are expressed in y^{-1}. R^2-values of the fitted curves are given.

Contaminant	Petroleum Harbour		Wemeldinge		k- values, results Chapter 4 and 5		
	k	R^2	k	R^2	fast	slow	very slow
PAHs	2.45	0.99	0.55	0.23	>3	0.15	0.03
Mineral oil	1.28	0.82	0.62	0.48	>0.8	0.17	

6.3.4 Effect of adding of substrate containing active fungi

Container experiments

The results of the container experiments showed that the addition of substrate containing the fungi *agaricus bisporus* leads to a lower residual concentration (see Table 6.3). However, the effects of substrate containing active (containers 1 and 2) and deactivated fungi were the same. The fungi activity did not give extra degradation. The extra degradation by the substrate could be caused by the improved soil structure, nutrients in the substrate or presence of extra dissolved organic matter (increasing of solubility of PAHs), but this was not investigated further. The substrate containing active and deactivated *Pleurotus spp.* did not give extra degradation. *Agaricus bisporus* and *Pleurotus spp.* from the substrate with active fungi did grow in the containers. Especially the *agaricus bisporus* developed well, even within lumps of sediment. The blank was the original sediment which had all the treatments except adding of the substrate containing the fungi. Probably the intensive mixing of sediment has stimulated the endogenous population to give a fast biodegradation of the PAHs. Already at t=0 the low concentration has been obtained. This fast decrease did not occur with the substrate. The easily degradable substrate has probably been preferred by the micro-organisms and they started degradation of PAHs later.

Table 6.3 Concentration (average of 5 measurements) and 95% confidence level of PAHs-concentrations (Dutch National List) in dewatered Petroleum Harbour sediment in the container experiments (corrected for added substrate).

Substrate	Concentration at start experiment (mg/kg d.m.)	Concentration after 24 days (mg/kg d.m.)	Decrease (mg/kg d.m.)
Agaricus bisporus (container 1)	32.4 ± 10.8	25.7 ± 11.0	6.7 ± 6.8
Agaricus bisporus (container 2)	33.2 ± 12	19.4 ± 2.9	13.8 ± 5.5
Agaracus deactivated	32.8 ± 12	23.3 ± 3.6	9.5 ± 5.5
Pleurotus spp. (container 1)	32.7 ± 6.7	33.6 ± 8.5	-0.9 ± 4.9
Pleurotus spp. (container 2)	30.3 ± 4.9	29.5 ± 8.5	0.8 ± 2.8
Pleurotus spp. deactivated	28.0 ± 1.2	29.5 ± 11	-1.5 ± 4.9
Only sediment	24.1 ± 3.2	24.4 ± 1.0	0 ± 1.5
Only sediment (duple)	24.2 ± 3.2	22.1 ± 2.2	1.8 ± 1.7

The extra degradation potential of substrate containing active fungi for high molecular and mineral oil by the fungi could also not be established. The results for *Agaricus bisporus* from Table 6.3 are further specified and presented in Table 6.4. This table shows that all ring systems and mineral oil are degraded in same extend with or without active fungi.

Table 6.4 Relative degradation (%) of different types of PAHs and mineral oil in a mixture of dewatered Petroleum Harbour sediment and substrate containing active and deactivated *Agaricus bisporus*.

Group of compounds	*Agaricus bisporus* + Petroleum Harbour sediment		
	Active fungi		Deactivated fungi
	Container 1	Container 2	
2 + 3 ring PAHs	19.9	49.5	36.9
4 ring PAHs	32.1	46.2	28.5
5 + 6 ring PAHs	18.8	24.2	14.5
Sum PAHs	20.6	41.7	29.0
Mineral oil	2.2	4.0	1.8

Hall experiments

In the Bion-hall it was investigated weather the fungi *Agaricus bisporus* and *Pleurotus spp.* could survive and be active under the conditions in the hall. The substrate (including the fungi) concentrations (by weight) in the Petroleum Harbour sediment were respectively 15 and 26%. The *Agaricus bisporus* added to the sediment was well developed. Development of *Pleurotus spp.* in the sediment could not visually be observed. Mushrooms from both fungi were growing after three weeks on the sediment/substrate mixtures. It was concluded that both fungi could survive and are applicable in a hall system.

Following this experiment, the effectiveness of the *Agaricus bisporus* substrate was tested on fresh sediment. After a fast dewatering period the fresh sediment was mixed with the *Agaricus bisporus* substrate. The results obtained in the first month presented in Figure 6.7 are a confirmation of the hypothesis shown in Figure 6.2. During dewatering of the sediment (first month) the bioavailable part has already been degraded. Mixing with substrate (containing active and deactivated fungi) and also a freshly prepared substrate instead of the residue of a mushroom farm, leads to the same decrease. Adding of all substrate had a positive effect on the bioremediation compared to both blanks. Again the presence of active fungi (Substrate in Figure 6.7) did not give an extra decrease, even not the very active fungi in the fresh substrate. Adding the same *Agaricus bisporus* substrates to soil from a gas factory also showed that in a period of two months no extra degradation occurs (data not presented, Harmsen *et al.*, 1999). It should however been mentioned that in the sediment as well as in the gas factory soil the fungi development was poor, probably caused by the bad soil structure.

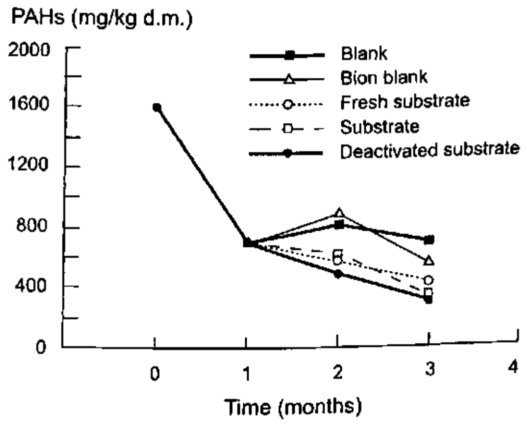

Figure 6.7 Decrease of PAHs-concentrations during different steps of the bioremediation. Time =0, original sediment; time =1 month, after dewatering and before adding of the substrate; time = 3 months, at the end of the experiment. Data points are the average of 5 measurements.

Field experiments

The field experiments were started in June 1997 (summer). Both substrate containing active (in different layer thicknesses) and deactivated fungi were used. Blanks were sediments with (Bion nutrients) and without nutrients. The temperature and moisture contents were not limiting factors until September 1997. This month was a very dry month leading to a very dry soil, about 17% moisture at the end of September compared to about 30% in August. Oxygen was also not a limiting factor with this sediment, although there was a remarkable decrease of the oxygen concentration in the gas filled pores in the first days after adding of the substrate (5% oxygen), caused by easily degradable substances in the substrate. Within the first month growth of mushrooms was observed. After two and four months it was not possible to detect *Agaricus bisporus* anymore. *Agaricus bisporus* has lost the competition with the endogenous microbiological population. All treatments have lead to comparable end concentrations; the fungi were not able to degrade the poorly available PAHs (Table 6.5).

Table 6.5 PAHs and mineral oil concentrations (average of 5 measurements) in mg/kg d.m. and the 95% confidence level measured on the landfarm. (corrected for added substrate).

Experiment	PAHs			Mineral oil
	2+3 ring	4 ring	5+6 ring	
time = 0, average all fields	12.3 ± 1.9	16.4 ± 2.1	13.6 ± 0.9	2400 ± 160
time = 4 month				
100 cm active	14.2 1.7	15.5 ± 4.6	13.5 ± 2.0	2410 ± 530
50 cm active	11.2 ± 2.6	11.6 ± 2.6	13.0 ± 1.5	2710 ± 100
30 cm active	10.4 ± 2.8	12.0 ± 2.0	12.4 ± 1.2	1900 ± 230
30 cm deactivated	10.1 ± 3.0	10.5 ± 2.3	11.1 ± 1.1	2100 ± 220
Only sediment	9.8 ± 2.2	10.3 ± 4.0	11.0 ± 1.2	2230 ± 140
Sediment with Bion nutrients	10.7 ± 1.7	11.4 ± 3.2	12.1 ± 2.1	2120 ± 100

6.3.5 Activation of microbiological activity in soil by vegetation

Fertilization of the sediment has, as to be expected, a positive effect on the plant growth (Figure 6.8). The effect is larger using grass than Lucerne. In Wemeldinge sediment the development of vegetation at the lowest nutrient level was pore. This is also caused by the pore soil structure of this sediment. More nutrients, however, compensated for this bad structure. Higher yields were obtained in the better developed (structure) Petroleum Harbour sediment.

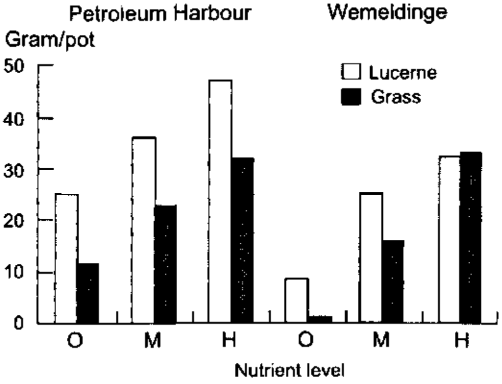

Figure 6.8 Vegetation development Petroleum Harbour and Wemeldinge sediment after different treatments. Nutrient addition 0 = no nutrients; M = medium and H = high (see also 6.2.4).

The results of the contaminant measurements in the different treatments are given in Table 6.6. Results of the landfarm Kreekraksluizen in the upper layer of the vegetated landfarm measured in October 1999 are also included in this table. The upper layer has been used for comparison, because concentrations in the lower layer are higher due to partly limited oxygen supply. Because differences are very small they are averaged for every nutrient level. If the treatment in the pots had an extra effect on the biodegradation of mineral oil and PAHs, the concentrations measured in samples from the pots should be lower than the concentrations measured in samples taken from the landfarm.

The mineral oil concentration in Petroleum Harbour in the pots of the vegetation experiment was further decreased than the mineral oil concentration in the landfarm. This decrease could be observed in all treatments. There was no relation with type or presence of vegetation or nutrient level (compare blank, Lucerne and grass). It is assumed that the activity of sampling the sediment on Kreekraksluizen, transport of the sediment, filling the pots for the vegetation experiment and optimum conditions in the glass house were responsible for the decrease and not the vegetation. The mineral oil concentration at the start of the experiment was still rather high and previously described activities could have created new oil surfaces, which are more easily degradable. Such a fast decrease was also observed after filling the containers described in Section 6.3.3. The level reached in the pots was reached on the landfarm in the following year. In the Wemeldinge sediment it was not possible to recognise a difference for mineral oil, but this level was already low and measurements on this level are less reliable.

No difference in PAHs-concentrations could be observed in the different pots (blank, blank + substrate, Lucerne and grass) at the end of the experiment. Concentrations were comparable with those measured on the landfarm in samples taken in the same period. The treatment in the pots did not lead to extra biodegradation (compared to the landfarm), which again confirmed that only the amount available for fast biodegradation has been degraded and not the slow and very slow available part.

The fractions of PAHs available for fast degradation measured in the pots (measured as fast desorbing fraction, Tenax-method) were low. For Wemeldinge sediment they were comparable with the values measured on the landfarm (see Chapter 4). The Tenax values measured for Petroleum Harbour in the pots were lower compared to the values on the landfarm, indicating that the intensivation led to a faster degradation of the available fraction. This is not only observed for the vegetated pots, but also in the pots without vegetation. Joner *et al.* (2001) also found a positive effect of the presence of arbuscular mycorrhizas (association between plant roots and fungi) on the degradation of spiked PAHs (available for fast degradation). Their extra reduction of available PAHs in presence of the mycorrhizas is in agreement with the reduction of fast available fraction measured with Tenax in our experiments.

Table 6.6 Mineral oil- and PAHs-concentration (Dutch National List) and the fast desorbing fraction (Tenax) at the end of the pot experiments (2.5 months) compared with the concentrations on the landfarm (vegetated upper layer) sampled on the same time. ( ) = standard deviation.

sediment	Nutrient addition	Vegetation	Mineral oil (mg/kg d.m.)	PAHs (mg/kg d.m.)	Fast desorbing fraction PAHs Tenax (%)
PH	0	blank	1780	25.5	3.3
			2010	25.2	3.3
	0	Lucerne	1780	22.7	2.1
			1440	18.7	2.3
	0	grass	2180	40.0	2.8
			1630	20.0	2.6
Average nutrient addition 0			**1803 (264)**	**25.3 (7.7)**	**2.7 (0.5)**
PH	M	blank	1700	35.5	3.3
			1770	27.7	4.8
	M	blank + substrate	1670	29.4	2.1
			1710	20.5	3.4
	M	Lucerne	1590	26.3	2.5
			1660	20.9	1.5
	M	grass	2050	21.5	4.7
			1620	14.7	3.8
Average nutrient addition M			**1721 (144)**	**24.6 (6.5)**	**3.3 (1.2)**
PH	H	Lucerne	2210	22.0	2.2
			2460	26.1	5.0
	H	grass	1830	18.9	5.0
			2150	23.3	3.4
Average nutrient addition H			**2163 (259)**	**22.6 (3.0)**	**3.9 (1.4)**
PH measured on landfarm (n= 5)			**3012 (205)**	**23.2 (3.3)**	**14.4 (11.4)**
WEM	0	blank	628	23.6	0.9
			613	18.3	0.5
	0	Lucerne	557	24.2	0.2
			406	32.3	0.6
	0	grass	498	26.8	0.5
			532	11.8	0.6
Average nutrient addition 0			**539 (81)**	**22.8 (7.1)**	**0.6 (0.2)**
WEM	M	blank	506	22.4	2.0
			489	23.6	1.5
	M	blank + substrate	573	21.7	1.4
			546	33.8	1.8
	M	Lucerne	540	32.3	1.0
			527	18.8	1.1
	M	grass	618	23.8	3.9
			469	20.5	
Average nutrient addition M			**534 (48)**	**24.5 (5.3)**	**2 (1)**
WEM	H	Lucerne	543	25.2	1.9
			459	34.8	4.0
	H	grass	577	24.7	4.5
			399	30.3	0.5
Average nutrient addition H			**495 (81)**	**28.7 (4.8)**	**2.7 (1.8)**
WEM measured on landfarm (n= 5)			**337 (42)**	**19.6 (4.3)**	**2.1 (0.8)**

The experiments in the pots have been continued till end of 2003 and vegetation was present during the whole year. The pots with Petroleum Harbour sediments were analysed again in 2003. Again no difference between the different treatments could be distinguished. The average value for the PAHs-concentration (National List) was 15.8 mg/kg d.m. (standard deviation 1.3 mg/kg d.m.). This is in line with the observation on the landfarm (Chapter 4). Based on first order decrease the actual degradation rate constant was 0.11 y^{-1}. In the vegetated landfarm the actual rate constant was 0.10 y^{-1} (see also Table 4.3 in Chapter 4).

Because there are no differences in the pots with and without vegetation, the vegetation has no influence on degradation of the residual concentration of PAHs and mineral oil still present in 1999. From Section 6.3.2 and the previous 2 chapters, it can be concluded that vegetation has a positive effect on degradation during the first years of landfarming. This effect however is indirect. In the first years the oxygen supply is the limiting factor for degradation. Vegetation has a positive effect on dewatering and improves the structure of the soil. This improves the oxygen supply and thereby the biodegradation.

6.3.6 Prediction of the fast biodegradable fraction PAHs

The fast desorbing fraction PAHs has been measured using the Tenax-method. This fraction has shown to be a good estimate for the fast degradable fraction. The results as fraction of the total concentration are presented in Figure 6.9. During the landfarming experiment the fast desorbing fraction in Petroleum Harbour sediment decreased from 80% in the original sediment to a few percent after 5 years. In Wemeldinge sediment the fast desorbing was already low in the original sediment (21%), but also decreased during landfarming. The fast desorbing fraction as prediction for the fast degradable fraction during landfarming as given in the subscript of Figure 6.9 is used to evaluate the effectiveness of the intensive treatments on the biodegradation of PAHs (see further).

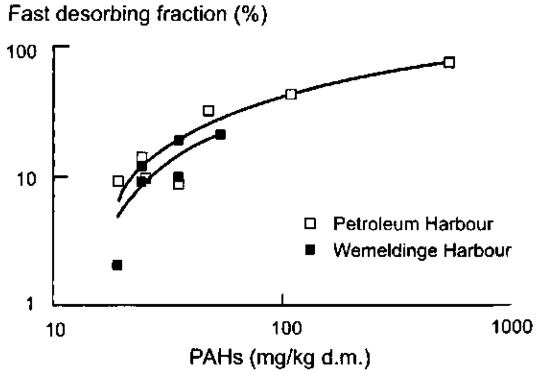

Figure 6.9 Measured fast desorbing fraction as function of the concentration in the (partly) remediated sediment. Petroleum Harbour ($y = 22.3 \ln x - 65.8$, correlation coefficient $R^2 = 0.87$); Wemeldinge ($y = 22.0 \ln x - 65.7$, $R^2 = 0.92$).

6.3.7 Results of published research on biodegradation of PAHs in Petroleum Harbour sediment

Dredged Petroleum Harbour sediment has also been investigated in different bioreactors. Results with Petroleum Harbour sediment are reported by Ferdinandy (1997) and Stefess (1997) using experiments performed by TNO, Bird Engineering and Arcadis. In all the reactor systems oxygen was actively supplied so dewatering was not necessary, this in contradiction to the optimised landfarm systems as described in previous sections. In the Slurry Decontamination (Bird Engineering) the complete dredged sediment was treated. The Aeration Basin (TNO) and the Continuous Bio Cascade (ARCADIS) utilized the fine fraction (respectively <63 and <20 μm). The fine fractions contained the main part of PAHs and mineral oil. Because new freshly dredged sediment from the harbour was taken for each experiment the results are also expressed as percentages of the initial concentration (Table 6.7).

Table 6.7 Bioreactor systems; bioremediation of original Petroleum Harbour sediment.

Treatment	Treatment time	PAHs			Mineral oil		
	days	Start mg/kg d.m.	End mg/kg d.m.	%	Start mg/kg d.m.	End mg/kg d.m.	%
Slurry decontamination process	5	350	30	91	9020	3200	65
Aeration basin	70	1050	84	92	14500	2400	83
Continuous Bio Cascade	9	1710	210	88	14600	4200	71

Using partly aerobic sediment from the Petroleum Harbour field with vegetation on the landfarm Kreekraksluizen (taken from lower layer), degradation also was not enhanced using the fungi *Bjerkandera* sp. strain BOS55 under optimum laboratory conditions. PAHs decreased in all treatments from 96 to 43 mg/kg (dry wt.) in a period of 8 weeks (Kotterman *et al.*, 1999)

6.4 Evaluation of degradation experiments

For the Petroleum Harbour sediment it is possible to compare all the different treatments as done in Figure 6.10. This figure is a combination of the PAHs degradation curve measured on the cultivated landfarm as presented in Chapter 4 (Figure 4.4) and the fast desorbing fraction or bioavailable fraction (Figure 6.9). The upper thick line is the total PAHs-concentration, the lower dotted thick line is the sum of the slow and very slow degradable fraction (total - fast desorbing fraction). The amount in between is the prediction of the amount that can be degraded on the landfarm in the following year. There is always a degradable part, because due to diffusion in soil particles not available PAHs become available again. Every year a new, but decreasing amount becomes available.

The effect of improved dewatering is showed by the degradation curve of the upper layer of the vegetated landfarm (curve is normalized to the original concentration in the cultivated landfarm). In this part oxygen was introduced most fast and full aerobic conditions were obtained within one year.

The results of experiments to optimize biodegradation by the use of a bioreactor, improved aeration + elevated temperature, adding of fungi and use of vegetation are presented in the same figure as lines, connecting the PAHs-concentration at start of the specific experiment and the obtained residual concentration. As described, these experiments were started during the landfarm experiment carried out on Kreekraksluizen. The concentration measured at the start of the specific experiment is plotted on the upper degradation curve and taken as starting point. The second point is the residual concentration obtained at the end of the experiment and plotted the treatment time of that specific experiment further to the right. The PAHs-concentration in the fresh sediments used in the bioreactor systems are normalised to the original concentration of the sediment on the landfarm. This figure makes it possible to evaluate the effectiveness of the application of a stimulation process on bioremediation in the Petroleum Harbour sediment. Because we could not measure the available fraction of mineral oil, such a figure could not be made for mineral oil.

Comparing the different stimulation experiments (short term) with the ongoing process on the landfarm (long term) as presented in Figure 6.10 and as presented in the section Results and Discussion, the profit of all stimulation is doubtful. Every action taken has shown to have a positive effect on the degradation rate, a lower concentration of PAHs has been obtained in a shorter time period. However, the same effect can be achieved on the passive landfarm, with a delay of one year. More specific it can be concluded that:

- A bioreactor gave the same result for both PAHs and mineral oil as a landfarm till the beginning of the passive phase (landfarming for 1-2 years). The available part of PAHs could be degraded including some of the slow available fraction. This is to be expected, because the rate constant for desorption in a slurry system is much larger than in the unsaturated landfarm as described in chapter 2 and 4. The duration of the experiments was long enough to make some of the slow desorbing fraction available. It takes more time on a landfarm to reach the same concentration, but landfarming is much cheaper than bioreactors.
- Faster dewatering on the landfarm to improve the aeration will result in a faster degradation of the fast available fraction. On the longer term (> 2 years) the same results are obtained in a slower dewatered sediment.
- Using forced aeration and a higher temperature after dewatering (1-2 years) removed only the residual available fraction. The available fraction, however, is already much lower than the fraction at the beginning of the treatment. Similar results were obtained in the same year on the landfarm, so the optimisation showed no benefit over landfarming after pre-treatment and dewatering.
- The same is true for the application of fungi; there was a stimulation of the bioremediation, but the properties of the substrate and not the fungi were responsible. Reid *et al.* (2002) has also reported stimulation of biodegradation using mushroom compost.
- An intensive vegetation (phytoremediation), applied after 4 years, did not give an extra degradation. Probably there will be a positive effect on the risks for soil organisms. Using the intensivated treatment the fraction available for fast degradation (= risk full concentration, see Chapter 7) seems to be lower, probably due to faster degradation of this fraction by a more active microbiological environment. Continuing the vegetation experiment in the pots for four years (till 2003) gave a decrease of the PAHs-concentration, but the degradation rate was the same as was measured on the outside landfarm.

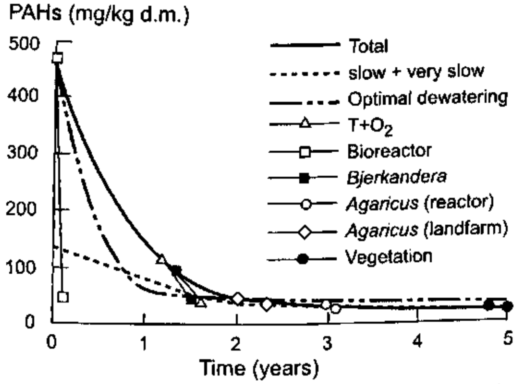

Figure 6.10 PAHs-concentration (Dutch National List) in Petroleum Harbour sediment landfarmed on Kreekraksluizen. The area between the total and slow + very slow degradable PAHs is an estimate of the fast degradable fraction of PAHs as measured with the Tenax procedure. Results of optimisation are plotted as lines connecting the concentration at start of the experiment with the concentration after finishing the experiment.

The evaluation described above shows that optimisation of landfarming does not give very improved results. With a little patience, the same results are obtained on a passive landfarm. However, if it is necessary to decrease the treatment time due to a low availability of surface area or due to the wish for timely reuse of the cleaned sediment, a more optimised bioremediation can be chosen. If so, removal of the fraction available for fast degradation must be sufficient to reach the target value. Treatment costs will increase as given in Table 6.8. Values in this table are estimates and depend on treatment time. Some of the methods are only applicable on dewatered sediment and the costs of dewatering have to be added. Costs for more optimised technologies are set by equipment, labour and energy. These items are less important for passive landfarming but in this case costs are set by the costs of the used land. Transport costs to the cleaning site are not taken into account for all treatments.

Table 6.8 Costs of bioremediation methods in Euro per ton dewatered sediment.

Bioremediation method	Type of sediment	Treatment time	Removal of degradable fraction	Costs/ ton dry matter
Bioreactor	fresh	1 – 3 weeks	fast	80
Hall treatment	dewatered	3 months	fast	30[2]
Application of fungi (hall)	dewatered	3 months	fast	30 +costs substrate
Dewatering	fresh	3-6 months	part of fast	15[1]
Intensive land-farming	fresh and dewatered	1-2 years	fast	30[2]
Passive landfarming	fresh and dewatered	>7 years	fast + slow	20[2]

[1] AKWA, 2001

[2] Personal communication P.Goedbloed and A van Ursem, Oostwaardhoeve, 2004

6.5 Conclusions

In this chapter results of optimisation of landfarming have been described. Results on the passive landfarm have been compared with different and more intensive treatments. Optimisation of the biological process on a landfarm is only possible if the conditions in the treated sediment are in agreement with the process to be stimulated. Conditions in the original dredged sediment differ completely from conditions in the soil developed during landfarming.

As long as the conditions are anaerobic, aerobic degradation cannot be stimulated. Active introduction of oxygen increases the rate of degradation as described in 6.3.6 for bioreactor systems. This is however a very intensive treatment, which can only be applied if costs of bioremediation are not the limiting factor. In a landfarm the active introduction of oxygen is not an option. Sediments have to become aerobic by dewatering and ripening of the sediment. A limiting factor for dewatering is the low permeability for water of the original sediments. In the Dutch climate, the sum of leaching and evaporation is not enough to dewater sediment. It is necessary to create a facility to discharge the excess of rainfall during the dewatering period. This can be achieved with small ditches. In combination with tillage and cultivation the fastest dewatering rate can be obtained (1 year or less for 1 meter of sediment). Increasing the rate of dewatering in a hall is not possible. Rainfall is prevented, but the evaporation rate is very low (100% moisture in the hall). Application of underpressure to increase the dewatering was also not effective. Dewatering using vegetation instead of cultivation is possible. It takes, however, a year for the vegetation to develop, resulting in a delay of about one year on the bioremediation process. Improper conditions for grow of vegetation (i.e. saline sediment) may give a further delay. With a high for fast degradation available fraction, as present in the Petroleum Harbour sediment, cultivation instead of vegetation gives a higher degradation in the first year (intensive phase of landfarming), but the long-term effect on end points concentration diminished in a few years. In sediment with a low for fast degradation available fraction (Wemeldinge) differences between cultivation and vegetation were not noticeable.

Optimising conditions for biodegradation as can be done in a bioreactor or a hall is effective for removal of the fraction available for fast degradation. If this fraction is large then the results seems to be effective, but if the supply of oxygen is not limiting, the same results can be obtained in a passive landfarm in one year.

Adding of a substrate with fungi in order to achieve fungi activity in the contaminated dewatered sediment is not always successful. Well-controlled conditions are necessary. With less optimal conditions, as present in a landfarm, the desired fungi disappear due to competition with the endogenous population of organisms present in the soil developed in the landfarm. This research shows that under controlled hall conditions fungal technology using substrates containing *Agaricus bisporus* and *Pleurotus spp.* will be favourable compared to outside conditions in a landfarm. These substrates may have a positive effect on the degradation of PAHs. However, the fungi are not responsible for the observed degradation. The same results could be obtained with substrates in which the fungi were deactivated. Therefore, full-scale remediation of a PAH contaminated vadose zone soil that could not be accomplished with native microorganisms but could be accomplished by augmentation using the fungi has not been demonstrated.

Use of vegetation (phytodegradation) to stimulate micro-organism activity by root-activity has been shown to have a positive effect on degradation. The fraction available for degradation degraded at a faster rate, but this did not lead to a lower residual concentration. As discussed before vegetation has an important role in dewatering and improving the structure of treated sediments.

Comparing the different stimulation experiments (short term) with the ongoing process on the passive landfarm (long term), all optimisations showed negligible benefits for biodegradation. All of the more intensive methods only stimulate biodegradation of the fraction of contaminants available for fast biodegradation. The same effect could be achieved with the passive landfarm, with a maximum delay of one year.

7 Environmental and ecological effects during landfarming of contaminated sediments

7.1 Introduction

Sediment (bagger in Dutch) contaminated with Polycyclic Aromatic Hydrocarbons and mineral oil, present perceived risks to the public. However, perception of risks is subjective. Risk can be defined as 'the possibility, with a certain degree of probability, of damage to health, environment and goods, in combination with the nature and magnitude of the damage' (Health Council of the Netherlands, 1995). This definition includes an uncertainty. As long as the magnitude of the uncertainty is not clear, decisions will be made on pseudo certainties; i.e., normative values prescribed in regulations. In that case, removal of the perceived risks will only be achieved when the contaminant has been completely removed.

In Dutch regulations (Staatscourant, 2000), remediation of a site is necessary when the intervention value has been exceeded. Above this value it is assumed that functional properties of soil for human beings, flora and fauna are seriously decreased or endangered. Intervention values are representative of serious soil pollution and are based on studies by RIVM (Lijzen *et al.*, 2001) on effects of soil pollution to humans and the ecological system. Human toxicological effects are based on Maximal Tolerable Risk Levels (MTR_{human}), which are equal to the Tolerable Daily Intake or the extra chance on tumour incidence of 10^{-4} in case of lifelong exposure (assumed that all exposure routes are operational). Ecologically, it is chosen to protect 95% of all species. This level is defined as the Maximum Tolerable Risk (MTR_{eco}), which means that the standard is chosen such that 95% of all the species show no- to the merest-observable sign of adverse effects. Ecological effects are often quantified as concentrations in the soil where 50% of the (potential) species and processes present may encounter observable negative effects. Using several organisms with different sensitivities and a statistical interpolation approach the MTR_{eco} can be calculated. The final intervention values for soil and sediment are based on integration of the human and ecotoxicological effects (in principle using the most sensitive of both).

Clean means that the concentrations of the contaminants are equal to or smaller than the reference value on which level sustainable soil quality is achieved. In practise this has been translated to the assumption that the reference values are indicative of the values that should be achieved to fully recover the functional properties of soil for human, flora and fauna. An overview of values for PAHs, and mineral oil in soil, sediments and water is given in Table 7.1. In 2002, in response to the governmental decision 'Policy renewal on soil remediation', a discussion has started that will lead to remediation objectives related to soil use and that will also be more risk-based (Van Wezel *et al.*, 2003).

Table 7.1 Reference and intervention values, HC_{50} and MTR for PAHs and mineral oil (Staatscourant, 2000).

PAHs	Water (µg/l)			Soil/sediment (mg/kg d.m.)			Human MTR
	Reference value		Intervention value	Reference value	Intervention value	HC_{50}	mg/kg body weight /day
	groundwater	surface water					
Dutch National List				1	40	40	
Phenanthrene	0.003	0.003	5				50
Anthracene	0.0007		5				50
Fluoranthene	0.003	0.005	1				50
Benz[a]anthracene	0.0001	0.0003	0.5				20
Chrysene	0.003	0.009	0.2				2
Benz[k]fluoranthene	0.0004	0.002	0.05				20
Benz[a]pyrene	0.0005	0.002	0.05				2
Benzo[g,h,I]perylene	0.0003	0.005	0.05				20
Indeno[1,2,3-c,d]pyrene	0.0004	0.004	0.05				20
Mineral oil	50		600	50	5000		1000

As shown in previous chapters, bioremediation of PAHs and mineral oil to reference value levels will not be achieved in the short term. Therefore, as long as the risk perception is correlated with the contaminant concentration, the contaminated sediment problem will not be solvable. It is necessary to show that bioremediation of contaminants will lead to a large reduction of risks, and that residual risks are on an acceptable level, even if residual concentrations of contaminants are present. A risk related assessment is necessary, which is intended to be part of future Dutch policy (VROM, 2004-a).

Instead of an assessment based on concentration of contaminants, a soil ecotoxicological risk assessment is promoted (Eijsackers and Løkke, 1996). When assessing ecological risks of chemical substances for soil ecosystems, one is faced with a threefold challenge (Eijsackers, 1997):

- How to access the impact of many compounds occurring simultaneously in variable compositions.
- How to encounter the considerable variance in environmental conditions, especially with respect to exposure and effects assessment.

- How to assess the impacts on a large variety of species, which have a heterogeneous distribution over a variety of ecosystems.

Kasamas and Vegter (2001) pragmatically describe risk assessment for contaminated sites from a more policy oriented view, i.e., as a loose assemblage of concepts and methods borrowed from various disciplines. Developments are being driven by regulators who need better decision-support systems. They conclude that the limitations of toxicological reference values, exposure modelling and soil and groundwater sampling are not widely understood and implemented in assessment studies. Integration and study of fundamental aspects of the various building blocks of risk assessment is said to be necessary.

In this study of landfarming of contaminated sediments the following risks have to be considered:

- Dispersion of the contaminant in the soil or to other systems such as ground water and surface water.
- Interaction of the contaminant with organisms living in the soil.
- Interaction of the contaminant with higher organisms that use soil, soil organisms or plant parts as food.
- Uptake of contaminant by plants.
- Ingestion by cattle and children.

In soil science, chemical, physical and biological functions of soil can be distinguished. Contaminants may influence them all. Under natural conditions, sediment deposited on land will develop in a soil, which quality depends on the physical and chemical composition of sediment. Most sediment will result in the development of a fertile soil, as can be observed in many delta regions in the world. Some sediments, however, containing very high amounts of clay particles (physical properties) or high amounts of sulphides (chemical properties), will develop into soil with undesirable properties: respectively heavy clay or acid soils. This must be kept in mind in evaluating the effects of contaminants. In table 7.2 these three functions are described and the possible influences of PAHs and mineral oil on these functions are indicated (second column). The third column gives the influence of the soil function on the contaminants.

Table 7.2 Relation between soil functions and the presence of PAHs and mineral oil.

Function	Influence contaminants on function	Influence function on contaminant
Chemical		
Retention of contaminants	-	+ **dispersion/leaching**
Physical		
aeration	-	+ degradation
water retention	-	+ **dispersion/leaching**
Biological		
Interaction with water living organisms	+ **toxicity**	
mineralization	+ **toxicity**	+ degradation
sediment/soil living organism	+ **toxicity**	+ degradation
Growing of vegetation	+ **food quality** and phytotoxicity	+ degradation

The bold marked functions in Table 7.2 are discussed in this chapter. The interaction of soil physical properties on soil aeration and the possible degradation of PAHs and mineral oil have been described in Chapter 2. Chapter 4 and 5 showed that sediments and soils functioned well in degradation of contaminants. In these chapters and in Chapter 6 it is shown that vegetation can grow and that phytotoxicity is not present.

The bold subjects relate to dispersion and to interaction with soil and water living organisms, as described in ISO 15799. In this guideline on ecotoxicological tests of soils, retention functions, and habitat functions are distinguished:

- Retention function - Ability of soils/soil materials to adsorb pollutants in such a way that they cannot be mobilised via the water pathway and translocated into the food chain.
- Habitat function - Ability of soils/soil materials to serve as a habitat for microorganisms, plants, soil living animals and their interactions (biocenoses).

Children, but also other higher organisms such as cattle, ingest soil during playing and grazing respectively. Effects on children of ingestion of sediment or soil are difficult to establish for ethical and practical reasons. Because landfarms for contaminated sediments are not playgrounds and will not be used for grazing cattle, these effects are only hypothetical and therefore not treated in this chapter. Effects on children and cattle will become important, if the soil in the future will serve a function where contact with children and cattle is possible. Examples of these functions are described in Chapter 9. Spreading of slightly contaminated sediment on land, on which cattle may graze, is described in Chapter 8.

In a landfarm, sediment changes into soil, this also implies that the population of species living in the landfarmed material will change. Sediment species will disappear and be replaced by terrestrial species. Especially in the first year after dredging the change in population is large and the sediment is colonized by soil living organisms (Eijsackers 2003). This will happen in both clean and contaminated sediments. Contaminants may have a negative effect on this development, but on Kreekraksluizen this has not been investigated for invertebrates.

Water plays an important role in the landfarm, especially as an intermediary to other environmental compartments. Figure 7.1 shows the risks in a landfarm as investigated on Kreekraksluizen: transport of contaminants to surface and ground water (retention function) and risks in the soil (retention and habitat function). The retention function can be evaluated with leaching experiments and experiments with aquatic organisms and the habitat function using experiments with plant growth and soil biocenosis. These tests are also distinguished as respectively acute and chronic bioassays (Van Gestel *et al.*, 2001). According to ISO 15799, these types of tests are of equal importance in soils used in green areas, parks, recreation areas and areas used in agriculture and horticulture.

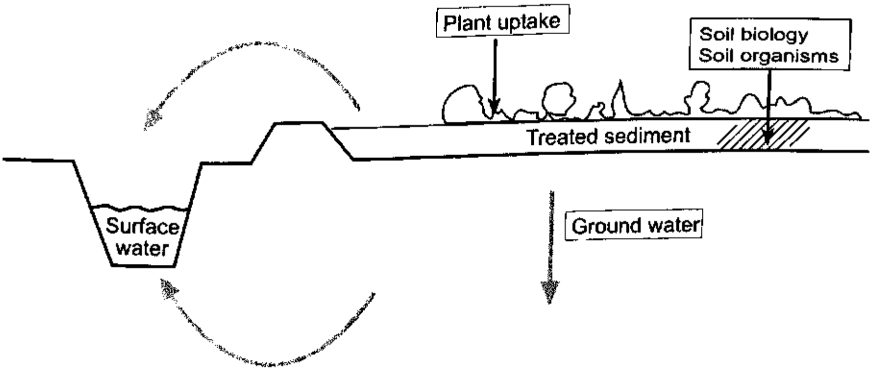

Figure 7.1 Environmental risks on a landfarm. Arrows are fluxes of contaminants in transported water.

7.1.1 Bioavailabilty

Chapter 3 has described the concept of bioavailability and the use of bioavailability in soil and site assessment. The conceptual definition of bioavailability used in relation to bioremediation as given in Chapter 3 can be slightly modified for risk assessment, with a distinction for respectively the retention and the habitat function:

- Bioavailability for the retention function means the amount of PAH and mineral oil that can be transported (caused by diffusion or physical change of the adsorption site) to a sediment/soil pore with mobile pore water.
- Bioavailability for the habitat functions means the amount of PAH and mineral oil that can be transported (by diffusion or physical change of the adsorption site) to a

site where an organism is present in a defined time period and that enters the bioinfluenced zone of this organism. It is the amount that is responsible for any effect on the organism.

This conceptual definition has to be made operational. Mobile pore water or leaching can be defined as the total amount in water that leaves the landfarm by drainage. This formulation is useful for risk assessment, because it includes the possibility of bioremediation. Using an operational definition based on the pore water concentration in the landfarm may overestimate the risks, because it excludes possible degradation during further transport in a site developed for bioremediation.

Related to the risks for organisms the operational definition of bioavailability for the habitat can be defined as effect (i.e., mortality, reproduction) measured within a monitored period. The results of these tests are a measure of the bioavailable concentration. The tools for measurement should be focussed on the retention function as well as the habitat function.

7.1.2 Retention function of soil

Transport via water of soluble, colloidal or particle fractions play a dominant role in the risk assessment of contaminated soils. This is true not only because water may mobilise contaminants, but also because contaminants and metabolites in the water phase have potentially a distinct effect on micro-organisms, plants and soil fauna. Aqueous eluates can be used to test the mobilisation or leaching, but can also be used for ecotoxicological effects on organisms exposed to the mobile water.

Leaching

The water phase may be responsible for leaching of the contaminant to the ground water system or to surface water. The solubilities of PAHs and mineral oil in water are low (see Chapter 2, Table 2.1). In combination with *DOC*, their solubilities may increase, however, as explained in Chapter 2. Also facilitated transport by colloids may play a role in transport of PAHs and mineral oil (Dolfing and Scheltens, 1999).

A measure to assess leaching can be the concentration in the water phase or in water produced during leaching tests (Van der Sloot *et al.*, 1997). Leaching tests are designed to provide a means of measuring the overall release of soluble constituents from a solid matrix (Heasman, 2003). Such an approach is very useful for heavy metals, as measurements are reliable and tests are already integrated in legislation. However, materials in the test and the test itself influence the results for PAHs and mineral oil. PAHs adsorb easily to equipment, thereby reducing concentrations. Contamination of the water samples with soil particles can be prevented in a laboratory study, but is difficult to prevent on the scale of the landfarm experiment on Kreekraksluizen. The concentration in the soil is much higher and the presence of only a few soil particles could influence the measured concentration in the water. Degradation of leached PAHs occurs already during the two days of a leaching experiment, especially at low concentrations, as can be expected during leaching test with soil (Steketee and Stefess, 2002). Leaching tests are developed for soil and waste, which are permeable for water. The low permeability of water in sediments will influence the practical development of a effective leaching test, thereby decreasing the reliability of such a test.

Water-dwelling organisms

To overcome experimental limitations with the chemical measurements in the water phase, it is also possible to focus on the active concentration in the water phase. This is the amount that affects water-dwelling organisms (i.e., the amount that is bioavailable for the test organism). In such an approach it is possible to take sediment samples instead of water samples. The sediment is brought into equilibrium with the water phase, and the water phase can be used for experiments with organisms. An equilibration time of 24 hours is usually used, which is sufficient (See also Chapter 3 and 4) to achieve equilibrium with the more rapidly desorbing fractions. Presence of a small number of solid particles will not influence the results. Bioassays normally used for testing water quality such as *Dapnia magna* and *Vibrio fisheri* can be used.

7.1.3 Habitat function

Effects on habitat function can be caused by the amount of contaminant in the water phase, but also by direct contact with the adsorbed contaminant. The presence of a large amount of mineral oil, which can even exist as a physical separate phase, can especially contribute to toxicity. The suitability of the soil for living organisms can best be examined by means of test methods selected to include organisms and processes representative of different taxonomic groups. Results of such a test have to be compared with those measured in non-contaminated soils (control). A control is preferably obtained close to and with the same soil type as the soils at the test site. This is not always possible; therefore also 'artificial' soils can be used. In testing, the different habitat functions of soil can be distinguished (ISO 15799):

- Soil as substrate for soil micro-organisms, which can be expressed in the mass of organisms or the result of their activity in soil (mineralization function expressed as nitrification and CO_2 production).
- Soil as substrate for plant growth, where tests have to be related with toxic effects and therefore have to be distinguished from tests in which accumulation in plant material or soil fertility is measured.
- Soil as substrate for soil-dwelling fauna, which have different functions in soil. Tests can be focussed on one of these functions. Soil animals generally fulfil the

> following four functions; (1) Mechanical activities (drainage, aeration, mixing); (2) Chemical changes (enhanced availability of nitrate and phosphate from excrements and accelerated formation of clay-humus complexes, after the substrate has passed the gut; (3) Biological changes (distribution of micro-organisms in the soil matrix, synergistic effects through stimulation of microbial activity and organic matter decomposition) and (4) significant links in the food web.

There is no single species that can be used for all of the listed functions. Therefore, the use of a battery of tests is necessary, taking into account the trophic level, different taxonomic/physiological groups, and ecological role (soil-dwelling and litter-inhabiting species). An important aspect in the choice of test organisms is the role of feeding. Sediment feeding organisms accumulate sediment-bound contaminants such as PAHs to much higher levels than organisms also living in the sediment but getting their food from suspension (Kaag, 1998). As mentioned before, ingestion of sediment or soil by children or cattle is not a part of this study.

7.1.4 Ecotoxicological methods

ISO 15799 describes several standardised terrestrial and aquatic test methods that have been developed to assess the ecotoxicological potential of chemicals (Table 7.3). Additional methods, recommended by other international organisations, are given by Loibner *et al.* (2003). These methods need to be adapted to the specific requirements of soil and site assessment. Some of these methods are already used in contaminated soils and are described further in this chapter. The effects on organisms used in bioassays are an indication of the bioavailability of contaminants for that specific organism. If such an organism is representative for a larger group, applicability increases. In ecotoxicological research a set of organisms is presently in use.

During landfarming, sediment changes into soil, due to ripening and dewatering. As mentioned previously, this results in a complete change in the population of species present, from sediment species to soil species. The biological development or activity of organisms can be used as indication for residual toxicity. Several methods have been used as described by Bloem (1995a-c). Parameters such as bacterial biomass, activity and diversity have higher values in a well-functioning soil ecosystem (Brookes, 1995). However, contamination does not always result in a decrease of biological activity. In some sandy soils a decrease of bacterial activity has been shown in the presence of heavy metals, but an increase has been shown in the presence of mineral oil (Díaz-Raviña and Bååth, 1996; Van den Munckhof *et al.*, 1998).

Table 7.3 Standardised biotest systems for ecotoxicological characterisation developed for testing of chemicals (ISO 15799).

Medium	Habitat	Organism/species	Effect
terrestrial	Soil	Spring tail, *Folsomia candida*	Reproduction
		Earthworms, *Eisenia foetida* or *Eisena andrei*	Acute toxicity
		Earthworms, *Eisenia foetida* or *Eisena andrei*	Reproduction
		Pot worms, *Enchytraeus spec.*	Reproduction
		Beetle, *Oxythyrea funesta*	Acute effects
	Soil	Barley, *Hordeum vulgare*	Root growth
		Monocotyledonous and dicot.plants	Emergency and growth
	Soil	Endogenous population	Mineralization and nitrification
		Endogenous population	Biomass
		Endogenous population	Ammonium oxidation
		Endogenous population	Soil respiration
Aqueous	Fresh water	Water flea, *Daphnia magna*	Inhibition of mobility
	Fresh water	Water flea, *Daphnia magna*	reproduction
	Fresh water	Unicellar algae	Inhibition of growth
	Fresh water	Zebra fish, *Brchydanio*	Acute toxicity
		Sharp ribbed newt, *Pleurodeles waltl*	Genotoxicity
		Duck weed, *Lemna minor*	Inhibition of growth
	Saline water	Unicellar algae	Inhibition of growth
	Saline water	Marine copepods	Acute toxicity
	Fresh and saline	Bacteria, *Vibrio fischeri*	Inhibition of luminiscence
		Bacteria, *Salmonella typhnerium*	Genotoxicity

Nematodes are the most abundant multicellular animals found in soils. They occupy key positions in soil food webs (De Ruiter *et al.*, 1995). Different groups of nematodes can be distinguished: bacterivores that consume bacteria; herbivores that extract food from living plants; fungivores that feed on the contents of fungal hyphea; predators that consume other nematodes; and omnivores that consume various food items. In a healthy soil system all groups are present. Counting different types of nematodes during landfarming can be used as an indicator for development of sediment into a soil (Bouwman and Vangronsveld, 2003). Counting of nematodes is also used to investigate the effect of contaminants (Doelman *et al.*, 1999 and 2000).

7.1.5 Risks and treatment on landfarms

To assess the success of bioremediation, the results of bioremediation will be compared with values set by regulators (see Chapter 1). These values are the reference values and the values mentioned in the Dutch Building Act. Several decades are necessary to reach the first value and several years to reach the second value (see

Chapter 4 and 5). Values for reuse of soils and sediments as building material were set as 40 mg/kg d.m. PAHs and 500 mg/kg d.m. mineral oil. In 2004 a regulation has been made by the Netherlands Ministry of Environment (VROM, 2004-b) to set the mineral oil value for reuse of sediments as 2000 mg/kg d.m. The Most important argument for setting these levels was that mineral oil in sediment does not contain the more volatile fraction, which is the most toxic fraction, which is in contradiction to the situation in soil. This change in policy will mean that a large quantity of sediments will be directly reusable as building material. This new value is a political compromise. Results of this chapter will show whether the new value is a real risk-based value. Whatever the target value will be, the large amount of sediment to be treated and the resulting large areas needed for landfarming make reuse necessary. This reuse will be only acceptable and sustainable when this can be achieved with an acceptable risk. Data on concentrations have to be replaced by data on risks.

Replacing total concentration by ecotoxicological testing does not imply that uncertainties are reduced. Different tests may give different results. This dilemma is formulated by Heise and Ahlf (2002) as follows: "The nature of ecotoxicological testing is in contrast with the long efforts to simplify natural systems and to look for numbers that ensure environmental quality. Ecotoxicology is a young field and much less straightforward than chemical analysis. Together with ecological data it reflects on the living environment. The degree of uncertainty is connected with the interpretation, and the deduction of risks from bio-tests is more obvious than with chemical quality criteria, where the process of estimating risks is a stringent procedure with no place for individual decisions. Therewith, an objectivity is feigned and reliability is confused with reproducibility".

Ecotoxicologists are still looking for an effective set of tests, ones that can be combined reliably with chemical information (Ahlf *et al.*, 2002). The Triad approach (Long and Chapman, 1985; Chapman, 1996, Rutgers *et al.*, 2001), a combination of sediment/soil chemistry, sediment/soil toxicity and resident community alteration, is used in the Netherlands to decide whether dredged harbour sediment can be discharged into the sea. Results of Triads are used in Biological Effect-Based Assessment (BEBA), but no standardised assessment is available. Different approaches used in Europe are described by Den Besten *et al.* (2003). Tests are being evaluated in round robin tests in order to develop proposals for standardisation of tests (Hund-Rinke *et al.*, 2002).

When the experiments described in this thesis were started (1990), the perception of risks was limited to leaching, which was a temporary risk on the landfarm, because it was assumed that bioremediation would lead to soil free of PAHs and mineral oil. The presence of a relatively high residual contaminant concentration has resulted in more risk-based research. The results of this risk-based research are presented in this chapter. Experiments on the used risk-evaluation tests in combination with the ongoing processes on the landfarm are discussed. This chapter is not meant to propose an optimal set of tests to establish the quality of cleaned sediments, as will be necessary when the present target values based on total concentrations is replaced by risk-based values. Results are used to get a better understanding of risks posed during landfarming in order to be able to make proper choices for a treatment procedure with minimal risks.

7.2 Materials and methods

The experiments described in this chapter have been carried out in combination with the degradation experiments on the landfarm Kreekraksluizen described in previous chapters. On the landfarm experiments have been carried out on (semi)field scale. The landfarm experiments were started in 1990. A limited number of experiments were carried out at the start of the Petroleum Harbour and Wemeldinge experiments in 1994 and experiments to evaluate the risk during landfarming were intensified from 1997 onwards. All landfarm fields, Geul Harbour (GH), Zierikzee (ZZ), Petroleum Harbour (PH) and Wemeldinge (WEM) were investigated. For Petroleum Harbour and Wemeldinge, both cultivated and vegetated fields were investigated. In the vegetated fields two layers were distinguished; an upper layer which was rapidly dewatered and a lower layer, in which dewatering took more time and contaminants were also slower degraded.

7.2.1 Retention function of soil

Leaching

The fields on Kreekraksluizen were supplied with a liner and drains. The extensive Geul Harbour and Zierikzee fields each had their own drainage system and could be sampled separately. For both the Petroleum Harbour and Wemeldinge fields, drains of the vegetated and cultivated fields were connected and these connected drains were sampled. Samples were taken during several field visits (if the drains discharged water), stored below 10 °C, and extracted with petroleum ether after arrival in the laboratory (within 24 hours).

An extra field without liner was constructed of 5 x 5 m containing Petroleum Harbour sediment. Instead of a liner, another soil protection system was tested consisting of soil enriched with organic matter (compost). The organic matter creates adsorption sites on which PAHs and mineral oil that leach could adsorb. Pore water has been sampled using porous ceramic cups with copper tubing (to prevent adsorption) in combination with vacuumed infusion bottles (Van den Toorn, 1999). All water samples were measured for PAHs and mineral oil after extraction with petroleum ether, using HPLC and GC-FID respectively, as described in Chapters 4 and 5.

Water-dwelling organisms

Bioassays were used to test the interaction of the contaminants with mobile water. Sediment or soil samples (Petroleum Harbour, Wemeldinge, Geul Harbour and Zierikzee) were taken and mixed with water. The bioassays were applied to water that was equilibrated with sediment and obtained after centrifugation. The bioassays used were *Vibrio fisheri* (Microtox) (NVN 6516, Maas *et al.*, 1993) and *Daphnia magna* (Maas *et al.*, 1993). Because Petroleum Harbour and Wemeldinge sediment were saline, the *Daphnia magna* test was only used in the sediments from the Geul Harbour and Zierikzee landfarm. The results of *Vibrio fisheri* are expressed as EC_{20}, which is the volume percentage of the original sample in the test sample, where bioluminescence has been decreased by 20%, compared to a blank, after a contact time of 30 minutes. A volume percentage of 45% is the highest percentage used, therefore an $EC_{20\text{-value}}$ of >45 means no effect measured, compared to the blank. Results of *Daphnia magna* are expressed in LC_{50}, which is the fraction (%) of the original sample in the test sample showing 50% mortality of the test organisms after 15 days (compared to control). Results are also expressed in the volume percentages showing no observed significant difference in mortality ($NOEC_m$) and reproduction ($NOEC_{repr}$) compared to the control.

7.2.2 Habitat function

Bioassays

Originally sediment was tested only using sediment organisms. Two types of organisms, for saline and fresh sediments, were used. After dewatering and ripening of the sediment, it was possible also to use soil organisms. Because salt was leached during dewatering and ripening, the same soil organisms have been used for all sediments. All organisms were soft skin organisms, which are thought to be more sensitive for contaminants (Vijver *et al.*, 2003). The test organisms used are described in Table 7.4.

Table 7.4 Bioassays used in the sediments.

	Saline sediments	*Fresh sediment*
Toxicity (sediment organism)	*Crassostrea gigas*1), PNR (percent net response) *Corophium volulato*3), mortality after 10 days	*Chironomus riparius*2), mortality, development and weight
Toxicity (soil organism)	*Lumbricus rubellus*3), survival, weight and reproduction *Folsomia candida*4), survival and reproduction	*Lumbricus rubellus*3), survival, weight and reproduction *Folsomia candida*5), survival, weight and reproduction
Bioaccumulation	*Oligochaetes*3) uptake of PAHs	*Oligochaetes*3) uptake of PAHs

1) Van den Hurk, 1991
2) Van den Hurk and Smit, 1991
3) Maas *et al.*, 1993
4) ISO 11268
5) ISO 11267

Biological development

Biological development was followed by measuring bacterial numbers and growth, genetic diversity, and development of the nematode population in samples taken on the landfarms. The total number of bacteria and the size of the cells were determined by direct microscopic counting (Bloem *et al.*, 1995a and b). For this purpose micro-organisms in soil samples were coloured with a fluorescent compound. Bio volume and biomass were calculated from the numbers and sizes. Confocal laser-scan microscope and automatic image processing were also used (Bloem *et al.*, 1995c). Samples were fixed and preserved with formaldehyde.

Bacterial rate of growth was measured using the incorporation of radioactive labelled ^{3}H-Thymidine and ^{14}C-Leucine into DNA and proteins respectively (Díaz-Raviña, and Bååth. 1996; Michel and Bloem, 1993). Because thymidine is labelled with ^{3}H and leucine with ^{14}C, both parameters (microbiological DNA- and protein syntheses) can be measured in one measurement. The relationship of rate of growth and incorporation of thymidine is more constant than in the incorporation of leucine. On the other hand, some anaerobic bacteria are not able to incorporate thymidine while leucine can be incorporated by most bacteria. Measurement of both is therefore supplementary. The incubations are short enough (one hour) to assure that the rate of growth does not change during incubation. In principle *in situ* rates of growth are measured. Biomass as well as rate of growth measurements can also be applied on anaerobic samples (Moriarty, 1986).

The genetic diversity of bacteria was measured using Denaturation-Gradient Gel Electrophoreses (DGGE) (Muyzer *et al.*, 1993). Microbiological DNA was extracted from the sampled sediment soil and multiplied with PCR (Polymerase Chain Reaction). The genetic composition of the DNA after using DGGE is visible in a pattern of bands. The number of bands reflects the number of genotypes (species), and the intensity of the band is a measure of the relative abundance of the group concerned. Patterns were analysed and quantified with an image-processing program.

Nematodes were isolated from the soil using Oostenbrinks elutriator (s'Lucas and van Bezooijen, 1984)). The isolated nematodes were counted using a stereomicroscope (3-fold) and identified under a 'high power' microscope. Nematodes are functionally subdivided into bacterivores, fungivores, herbivores and onmivores/predators, as related to their choice of food: bacteria, fungi, plant roots and animal organisms (predators) or a broad spectrum of food (omnivores). They can be distinguished by the structure of their mouth. With a normal diversity, 150 specimens were identified. With a low diversity, when most nematodes belonging to one taxum, 450 specimens, were identified.

7.3 Results and discussion

7.3.1 Retention function of soil

Leaching

During the entire experimental period at Kreekraksluizen it has never been possible to smell mineral oil in the drainage water. In all water samples taken the mineral oil was below the detection limit (50 μg/l). PAHs were detectable, but their concentrations were very low (Table 7.5).

Drainage water samples from Geul Harbour and Zierikzee sediments were taken and analysed in the autumn after the passive landfarm was started (1993). In this first passive treatment period there were still some anaerobic sections in both sediments that could prevent degradation and lead to leaching. Also the transport of the sediment to the new passive fields (see Chapter 4) could have led to facilitated transport by organic matter or colloids. PAHs could not be detected in the drainage water samples taken (Table 7.5) showing that in these landfarms leaching did not occur. The detection limits presented in this table are not constant for each individual PAH, but are caused by the different amounts of water that could be obtained and the background signal in the chromatogram. From 1990, the PAHs-concentrations measured in the basin, where drainage water was collected, was low enough (6 of Borneff < 0.1 μg/l) to permit discharge of this water to the surface water system (Daemen, 2004, Personal communication).

During the intensive phase of landfarming, the values measured in the drains of the Petroleum Harbour and Wemeldinge fields were mostly below detection limit, but were sometimes detectable. The measured values (Table 7.5) were far below the intervention value defined in the Netherlands (Table 7.1) and are comparable to but also slightly higher than the reference value. Below the reference value no negative environmental impact is to be expected. For PAHs, the reference value is not based on real measured values, but obtained after extrapolation. The detection limit of most analytical methods for PAHs is much higher than the reference value. The measured values were also low enough to discharge the drainage water of the Petroleum Harbour and Wemeldinge fields to the surface water system.

Tabel 7.5 PAHs-concentrations in drainage water (μg/l).

PAHs	Sampling date (month-year)										
	Geul Harbour	Zierikzee	Petroleum Harbour			Wemeldinge			Mixed PH + WEM[1]		
	10-93	10-93	8-94	2-96	12-97	9-94	2-96	12-97	9-96	11-96	11-97
Fluorene	<0.02	<0.02	<0.1	0.033	0.002	<0.1	0.009	0.002	<0.02	<0.005	<0.008
Phenanthrene	<0.01	<0.01	0.02	0.012	0.016	0.06	0.02	0.02	0.02	<0.01	<0.001
Anthracene	<0.001	<0.001	0.002	<0.002	<0.001	0.001	<0.002	<0.001	0.003	<0.002	<0.001
Fluoranthene	<0.01	<0.01	<0.02	<0.04	0.004	<0.02	<0.04	0.004	<0.02	0.02	<0.001
Pyrene	<0.04	<0.04	0.006	<0.03	<0.005	0.01	<0.03	<0.005	0.008	<0.01	<0.005
Benz[a]anthracene	<0.008	<0.008	<0.001	<0.005	<0.004	<0.001	<0.005	<0.004	0.006	<0.004	<0.004
Chrysene	<0.009	<0.009	0.001	<0.008	0.001	0.001	<0.008	0.001	<0.008	<0.005	<0.001
Benz[b]fluoranthene	<0.003	<0.003	<0.001	<0.01	<0.001	0.001	<0.01	<0.001	<0.01	<0.005	<0.001
Benz[k]fluoranthene	<0.001	<0.001	<0.001	<0.01	<0.001	<0.001	<0.01	<0.001	<0.01	<0.005	<0.001
Benz[a]pyrene	<0.004	<0.004	<0.001	0.004	<0.003	0.001	<0.004	<0.003	0.009	<0.005	<0.003
Benzo[g,h,i]perylene	<0.03	<0.03	<0.002	<0.02	<0.002	<0.002	<0.02	<0.002	0.03	<0.005	<0.002
Indeno[1,2,3-c,d]pyrene	<0.01	<0.01	<0.02	<0.05	<0.005	0.002	<0.05	0.01	<0.04	<0.005	<0.005

[1] Because it was not always possible to obtain enough water on some dates, the drainage water from both sediments have been combined

In the field with an organic matter-enriched soil layer as soil protection, water was collected with porous cups. The results of the PAHs analyses are presented in Table 7.6. It was difficult to obtain water from the protection layer. This is caused by the low permeability of the sediment for water as described in Chapter 6. In order to increase the sensitivity of the measurement, the sample size was increased by combining water from all installed cups into one sample. In the first sample collected, the PAHs concentration had increased. This water sample was turbid and contained colloidal particles. Later samples collected were always clear. It is assumed that when water is collected from the cups by applying under pressure, water collected is combined with some sediment particles. The colour was always brown, which is caused by dissolved organic matter originating from the added compost. Also in these samples the measured PAHs values were low. Only concentrations of the heavy PAHs were in some cases near the intervention value. The reliability of these measured values is low, however, because confirmation of the measured values was not possible due to the low concentration. The most sensitive wavelength combination on the fluorescence detector was necessary to measure these values; other combinations were less sensitive.

Table 7.6 PAHs-concentrations in pore water in the drainage layer (μg/l). Field with extra organic matter as soil protection (Petroleum Harbour sediment).

PAHs	Sampling date (month-year)					
	8-94	9-95	11-95	1-96	6-97	8-97
Fluorene	<0.5	0.1	0.002	0.004	0.006	0.01
Phenanthrene	0.2	0.04	0.01	0.02	0.01	0.01
Anthracene	0.008	0.005	0.001	0.001	0.001	0.004
Fluoranthene	0.1	0.05	0.005	0.009	0.02	0.05
Pyrene	0.06	0.01	0.004	0.009	0.009	0.04
Benz[a]anthracene	0.008	0.003	0.003	0.004	0.003	0.006
Chrysene	0.04	0.09	0.006	0.009	0.002	0.007
Benz[b]fluoranthene	0.009	0.008	0.002	0.009	0.01	0.01
Benz[k]fluoranthene	0.003	0.003	0.001	0.006	0.005	0.01
Benz[a]pyrene	0.005	0.02	0.001	0.008	0.008	0.03
Benzo[g,h,i]perylene	<0.01	<0.01	0.01	<0.009	0.005	0.02
Indeno[1,2,3-c,d]pyrene	0.01	<0.01	<0.002	0.03	0.02	0.06

From 1997, the passive landfarming concept was applied on a practical scale on Oostwaardhoeve in combination with growing of biomass (see Chapter 9). Based on the results on Kreekraksluizen (Harmsen *et al.*, 1996 and as presented in this chapter), the liner as soil protection was replaced by organic matter already present in the soil on this site (see also Section 7.3.3 in this chapter). After the first sediment treatment in 1997, different sediments were treated on different fields up to a total surface of 10 ha. The water from the drain tubes in the fields discharged water to a collection basin. This water, which was discharged to the surface water system, has been analysed from 1997 to 2003. No increased concentrations of PAHs and mineral oil could be detected (Goedbloed, 2003, Personal communication). All PAHs concentrations were below 0.02 μg/l and mineral oil concentrations below 50 μg/l. Pleijte (1996, Personal communication) had similar results while treating PAHs-contaminated sediment on a site near Julianadorp.

Water-dwelling organisms

Because it is difficult to separate the water phase from the sediment without losses of PAHs and mineral oil, the presence of bioavailable contaminants in the water phase was tested with bioassays. *Vibrio fischeri* showed toxicity ($EC_{20} < 45$) in the original Petroleum Harbour sediment and during the first year (1994) of landfarming (Table 7.7). No toxicity (except one outlier in 1997) was measured in following years. *Vibrio fischeri* did not show toxicity in Wemeldinge sediment. As described before, the test was not performed on the Geul Harbour and Zierikzee sediment during the intensive phase (1990-1993). Toxicity was present at the beginning of the passive phase, after transport of the sediments to the passive fields. All subsequent samples did not show toxicity. This means that toxic compounds were not present in a concentration in the water phase to be toxic for *Vibrio fischeri.*

Table 7.7 Results of *Vibrio fischeri* (EC_{20} (%v/v)) in water obtained from different landfarmed sediments (see also Chapter 4).

Sediment	sampling period (month-year)	EC_{20} (%v/v)		sampling period (month-year)	EC_{20} (%v/v)	
		Petroleum Harbour	Wemeldinge		Geul Harbour	Zierikzee
Fresh	8-94	8.4	>45	5-94	13.4	34
Vegetated upper	10-94	30	>45	6-95	>45	>45
Vegetated upper	6-95	7.6	>45	10-95	>45	>45
Vegetated upper	12-95	1.0	>45			
Vegetated lower	10-97	>45	>45	10-97	>45	>45
		>45	>45	10-99	>45	>45
Vegetated upper	10-97	>45	>45			
		>45	>45			
Cultivated	10-97	>45	>45			
		17.6	>45			
Vegetated upper	10-99	>45	>45			
Vegetated lower	10-99	>45	>45			
Cultivated	10-99	>45	>45			

Comparable results with *Daphnia magna* (Table 7.8) were obtained in the non-saline Geul Harbour and Zierikzee sediment. The toxicity measured in the sample of Geul Harbour from 1997 is considered to be an outlier.

Results of both bioassays are in agreement with the low concentrations of PAHs and mineral oil measured in the drainage water and in the pore water below the sediment, as described in 7.3.1.1. PAHs and mineral oil were still present in the solid phase and can desorb and diffuse to the water phase. The rate of this process will not be rapid enough to cause toxicity. Another explanation is that in the aerobic test system and on the aerobic landfarm, the toxic compounds are degraded before they can be responsible for toxicity.

Table 7.8 Results of *Daphnia magna* in water obtained from Geul Harbour and Zierikzee sediments.

Sampling	Geul Harbour			Zierikzee		
date (month-year)	LC_{50} (% v/v)	$NOEC_m$ (% v/v)	$NOEC_{repr}$ (% v/v)	LC_{50} (% v/v)	$NOEC_m$ (% v/v)	$NOEC_{repr}$ (% v/v)
5-94	>100	100	100	>100	100	100
6-95	>100	100	100	>100	100	100
10-95	>100	100	-	>100	100	100
10-97	>100	56	< 10	>100	100	100
10-99	>100	100	100			
Blank	>100	>100	100	>100	>100	100

Consequences of observed leaching for soil protection

As a result of the experiment on the retention function of soil and especially on leaching, another concept of soil protection has become possible. Before this study, liners were thought to provide the most effective soil protection and were prescribed in most situations where contaminated sediment or soil has to be handled. They were assumed to prevent all leaching of contaminants, but this was not based on research in field situations. A liner also has several limitations:

- It is necessary to have a drainage layer between the liner and the sediment to stimulate dewatering and aeration. Water-saturated conditions will be present just above the liner.
- A liner is not watertight. Leakages will occur through holes caused by sharp particles or due to the heavy machinery used during intensive landfarming and removal of the cleaned sediment. A liner under field conditions is usually not completely impermeable due to mistakes in welding. Under ideal conditions, up till 20 holes of 1 cm^2 will be present per hectare (Boels, 1993). In a landfarm extra holes will be created during use and one hole per 10 m^2 seems to be more realistic. This will lead to a leakage of 10 to 20% of the rainwater surplus.
- Liners are not impermeable for organic chemicals. Breen and Der Kinderen (1991) showed that benzene and toluene were only retained 1 to 10 weeks. Larger molecules will be retained longer.

The above considerations illustrate that a liner is not the ideal soil protection to be used in a landfarms and the effectiveness of different means of soil protection should be evaluated.

A good soil protection system will retard the eventual transport of contaminants. As shown above, a liner has to be combined with a drainage layer, which may give further retardation of the contaminant. This retardation is greatly dependent on the organic matter content; the relative transport velocity can be described as:

$$v_i / v_w = \varepsilon_w / (\varepsilon_w + f_{oc} K_{oc} \rho)$$

where:

v_i = mobility of the contaminant (m/y)
v_w = velocity of the pore water (m/y)
ε_w = fraction water filled pore volume
f_{oc} = fraction organic carbon
K_{oc} = partition coefficient organic carbon and water
ρ = density of dry soil (kg/l)

K_{OC}-values for PAHs are much larger than ε_w even when the association with organic matter is taken into account (see Chapter 2). This means that the relative transport of PAHs becomes inversely proportional to the fraction of organic matter. In drainage sand this fraction is about 0.1 percent. Using organic matter such as compost, this percentage can be easily increased to a few percent. Another approach is to deposit and further treat the contaminated sediment on top of original agricultural soil, which has naturally high organic matter content. Decrease of the relative transport velocity of a factor of 10 to 30 can be easily obtained. The most mobile PAH, naphthalene, has a relative transport velocity of 0.016 in a soil with 2% organic matter, a fraction of water-filled pore volume of 0.5 and a density of 1.6 kg/l. With a yearly rain fall surplus of 300 mm (normal under Dutch conditions), this means that for transport of naphthalene over a distance of 30 cm, about 20 years will be necessary, while much more time will be necessary for the more heavy PAHs. The K_{oc}-value of these PAHs is at least a factor of 10 larger, even when the association with dissolved organic matter is taken into account. Resulting transport times of more than 200 years for most PAHs are greater than the guaranteed life time of a liner.

On the landfarm Kreekraksluizen, a drainage layer with low organic matter content (<0.1%) showed no leaching during the treatment period (1990-2001). Retardation using organic matter could therefore be an effective soil protection system for the longer term, especially if this will occur in combination with biodegradation of PAHs. The latter can be achieved by using a drainage system that not only removes excess water, but also introduces oxygen, or by locating the landfarm on a permeable soil containing sufficient oxygen. Soil protection without a liner requires a zone for retardation of leached contaminants (organic matter) and a zone for degradation of these contaminants. Both zones can be combined. The organic matter present in the protection layer should not fully degrade during remediation of sediment, which may require several decades (see Chapters 4 and 5). Natural organic matter in soil is slowly degradable, as shown in Table 2.5 of Chapter 2. Using materials such as compost, degradation of organic matter has to be taken into account to ensure that the organic matter content remains sufficient high during use of the landfarm.

This method of soil protection has been applied on a following large scale landfarm on Kreekraksluizen started 1995 (De Bruyckere en van der Linden, 1995) using peat to increase the organic matter content in the subsoil to 3%. On the Oostwaardhoeve the soil present contains already 3% organic matter and was used as soil protection as without the need for addition of organic matter. The hydrological situation at this site is such as to prevent leaching risks. It is situated in a polder and a light seepage is present. All drainage water flows to the ditch system of the farm and finally to a large basin. From this basin, it is pumped to the surface water system. This is the only off-site water flow and can be controlled. So no risks are present for the groundwater system and the surrounding surface water (Figure 7.2).

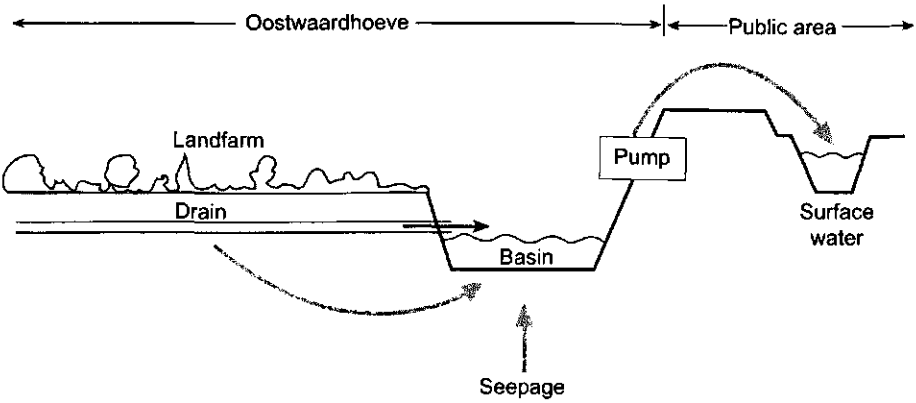

Figure 7.2 The hydrological system on Oostwaardhoeve.

7.3.2 Habitat function

Sediment assays

Crassotrea gigas and Corophium volulator

From the start of the landfarming experiment with Petroleum Harbour and Wemeldinge (1994 till 1997), sediment bioassays with soft skin sediment organisms have been used. The results with *Crassotrea gigas* and *Corophium volulator* are presented in Table 7.9. The toxicity of Petroleum Harbour sediment at the start of landfarming is larger than the toxicity in Wemeldinge sediment, which is in agreement with the higher PAHs and mineral oil concentrations. The decrease in toxicity appears to be the lowest in the lower layer of the vegetated landfarms, which is also the layer with the slowest degradation. The lower toxicity in the other samples in which higher biodegradation is observed, indicate that biodegradation may have a positive effect on the residual toxicity.

Table 7.9 Results of bioassays using sediment organisms (all individual measurements).

Sediment	Sampling Period (month-year)	*Crassostrea gigas* (PNR) (%)		*Corophium volutator* (mortality) (%)	
		Petroleum Harbour	Wemeldinge	Petroleum Harbour	Wemeldinge
Fresh	8-94	99.3	39	100	77
Vegetated upper	10-94	99	16	100	18
Vegetated upper	6-95			100	5
Vegetated upper	12-95			100	5
Vegetated upper	10-97	99; 98	11; 17	70; 81	12; 7
Vegetated upper	10-99	82		48	
Vegetated lower	10-97	100; 93	26; 21	97; 100	13; 10
Vegetated lower	10-99	85		36	
Cultivated	10-97	56; 61	20; 5	18; 16	5; 7
Cultivated	10-99	43		20	
Blank		-5.4	-5.4	4.5	4.5

Toxicity can be caused by different contaminants present in the sediment (PAHs, mineral oil, but also slightly increased heavy metal content). The latter can be responsible for a residual toxicity after biodegradation of the PAHs and mineral oil. In Figure 7.3, the toxicity observed in the different fields is plotted against PAHs- and mineral oil concentrations. The two sediments have comparable residual PAHs concentrations. The lower effect values of Wemeldinge are comparable with the values for Petroleum harbour. The resulting figure for both bio-assays has the shape of a normal dose-response curve and the no effect value is close to the residual concentration of 20-25 mg/kg d.m. for both sediments. This value is far above the reference value and has the same level as the intervention value; respectively 1 mg/kg d.m and 40 mg/kg d.m. at 10 % organic matter. The organic matter in the tested sediments varied between 5 and 8% (see Chapter 4.3.3).

Using the mineral oil concentration as the factor that explains toxicity, the no effect value for the test organisms is also equal to the residual concentration as present in 1999. The no effect values for both sediments are different; about 2000 mg/kg d.m. for Petroleum harbour sediment and less than 1000 mg/kg d.m. for Wemeldinge.

From the two figures it can be concluded that during bioremediation, different contaminants present in the sediment can cause toxic effects. It was not possible in this experiment to distinguish between the toxic effects of PAHs and mineral oil. Both contaminants may have influenced the no effect value found for the individual contaminants.

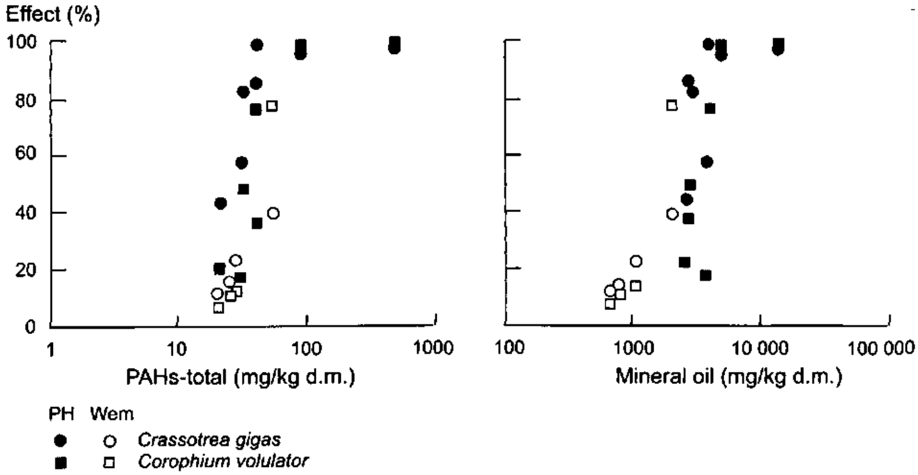

Figure 7.3 Results of the bioassays with *Crassotrea gigas* and *Corophium volulator* as a function of the PAHs-concentration (left) and mineral oil concentration (right) in the tested sediments. Closed signs Petroleum Harbour, open signs Wemeldinge.

Another way of evaluating the observed toxicity is in relation to availability. Tenax extraction mimics the availability for several benthic and terrestrial organisms (Ten Hulscher *et al.*, 2003). The available PAHs-concentration in the tested sediments is estimated using the Tenax-procedure which measures the amount of PAHs available for fast desorption and can be used to predict the amount biodegraded on a landfarm (see Chapter 4). The amount available for biodegradation is also derived from the degradation curves presented in Chapter 4. The biodegradable amount (degradable in one year) is calculated for the moment the samples were taken for testing. Results are presented in Figure 7.4. On first analysis, the range for the Tenax-available PAHs is wider than the biodegradation data and the data presented in Figure 7.3. However, this does not mean that the results of the Tenax-procedure are less well correlated with the effects of the bioassays. The wider range is mainly caused by the larger uncertainty of the Tenax-results at low available fractions. Below an available fraction of 10% of the total amount, the standard deviation of the Tenax-method is of the same order of magnitude as the measured value (see Table 4.5 in Chapter 4). It is therefore necessary to improve the Tenax measurement at low available fractions. Application of the degradation rate results in a no effect value of approx. 3 mg/kg d.m. available PAHs. This value is close to the reference value, which should to be considered as a value where no toxic effect occurs.

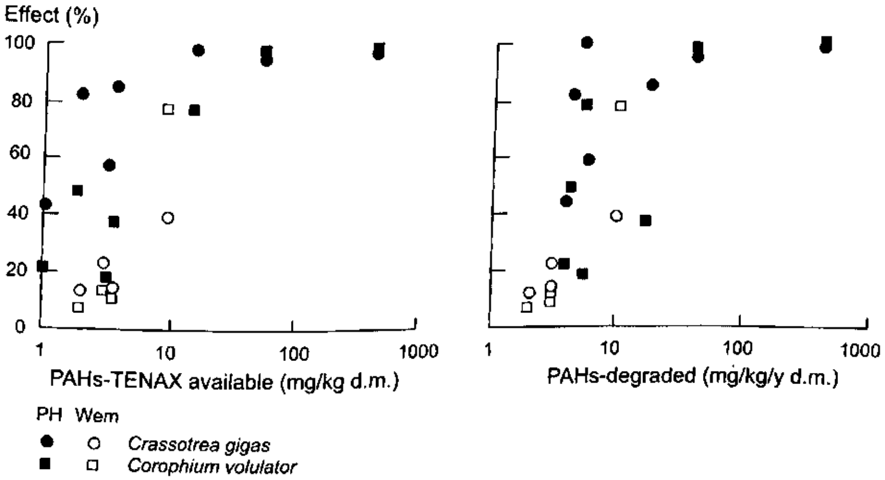

Figure 7.4 Results of the bioassays with *Crassotrea gigas* and *Corophium volulator* as a function of the available PAHs. Available for fast desorption (Tenax) in left figure and available for fast biodegradation in right figure. Closed signs Petroleum Harbour, open signs Wemeldinge.

Chironomus riparius

For the Geul Harbour and Zierikzee sediments, results of sediment bioassays with *Chironomus riparius* are available since 1994, four years after the start of the landfarm treatment. Results are presented in Table 7.10 and show that residual toxicity is present in the period 1994-1997 and did not decrease. Large effects were not been measured, but are to be expected when the assay was applied on the original fresh sediments (comparable with the results presented in Table 7.9). Because the availability of the contaminants in the aerated sediment was small and still decreasing, a decreasing toxicity was expected.

The applicability of the test organism, given the experimental set-up on the landfarm, has to be assessed critically. During the sampling period, Geul Harbour and Zierikzee sediments were completely dewatered and transferred to a soil. *Chironomus riparius*, an aquatic organism, was introduced in a system containing a layer of soil covered with water. The soil thereby changes from aerobic to anaerobic. Properties of the soil will change accordingly, which may result in a change of bioavailability of contaminants present (including heavy metals) or in the formation of toxic compounds. Therefore it was decided to change to bioassays using soil organisms for further testing of the treated sediment (see further in this chapter). Initially tests with soil organisms were run parallel to experiments with sediment organisms in 1997.

Table 7.10 Results of the bioassay *Chironomus riparius* in treated Geul Harbour and Zierikzee sediment.

Sediment	Sampling Period (month-year)	Mortality (%)	Development, mortality + stage (%)	Dry weight, relative to blank (%)
Geul Harbour	5-94	12	25	-18
	6-95	10	27	-24
	10-95	15	36	-23
	10-97	28	51	-24
Zierikzee	5-95	29	41	12.6
	6-95	21	29	-18.4
	10-95	29	52	0.5
	10-97	14	46	-23.7
Blank (10-97)		7	18	

Bioaccumulation

Bioaccumulation has been tested since 1997 with aquatic oligochaetes living in the sediment. These organisms obtain their food from the anaerobic sediment. Accumulation of PAHs in these organisms is an indication of the bioavailability of PAHs. The accumulation in the oligochaetes is presented in Figure 7.5. The sediments are arranged in order of the amount of fast available PAHs, as can be estimated using the Tenax-method, or the amount degraded in one year (both had also been measured in 1997). These amounts were the highest in the sediments that were still partly anaerobic in 1997, i.e., in the lower layers of the vegetated landfarms. Accumulation of PAHs in the oligochaetes in these sediments was high. No accumulation occurred in the Geul Harbour and Zierikzee sediments, where the available amounts of PAHs are very low.

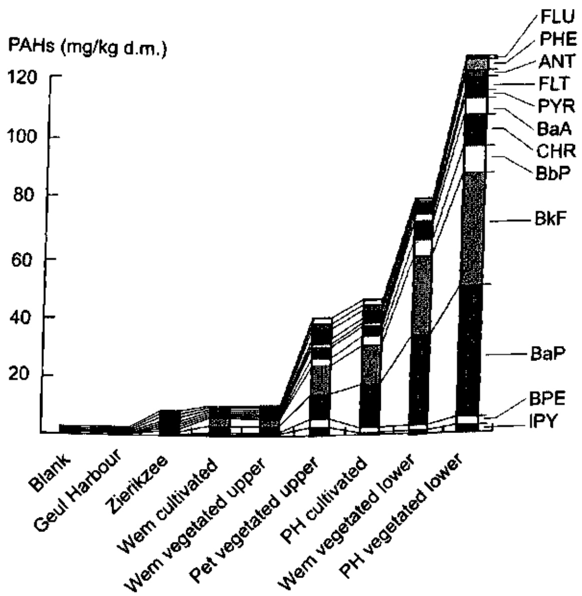

Figure 7.5 Accumulation of PAHs in oligochaetes exposed to the treated sediments in 1997. Sediments are arranged in order of increasing amount of fast available PAHs.

Soil assays

Earthworms are commonly used organisms in testing soils, both to study toxicity and bioavailability (Jager, 2003). Conditions in sediments (anaerobic) are not a suitable environment for earthworms and they are not found in freshly dredged sediment. Although earthworms can survive in soil becoming water-saturated for a winter period (Zorn, 2003), they are not a logical choice to be used as a bioassay in fresh sediment. The water-saturated and anaerobic conditions in the sediment would influence the results too much. After dewatering and ripening, the limiting conditions for survival disappear and application of this soil bioassay is possible.

In 1995 earthworms (*Lumbricus rubellus*) were used in bioassays applied to Geul Harbour and Zierikzee sediments and from 1997 onwards also on Petroleum Harbour and Wemeldinge sediments. Results are given in Table 7.11. In 1995 this bioassay showed no residual toxicity in the oldest treated sediments (Geul Harbour and Zierikzee). Similar results were obtained in 1999 and 2001. In these sediments both PAHs and mineral oil concentrations are low. Based on the total PAHs concentration (compared to the reference value) in Zierikzee sediment, toxicity could have been expected, however, but the available PAHs fraction is low.

Survival is the least sensitive parameter; only in the most contaminated samples, i.e., the lower layer of Petroleum harbour sediment, a reduced survival is observed. More sensitive parameters are weight increase and reproduction, as measured by the number of cocoons found. At low available PAHs concentrations there is no effect on reproduction (Geul Harbour and Zierikzee). This has also been shown by Eijsackers *et al.* (2001) for PAHs-contaminated dredged sediment. They also showed that addition of fresh PAHs decreased reproduction. On the other hand, they observed that the earthworms had a positive effect on the degradation of PAHs.

Table 7.11 Results of the bioassays with *Lumbricus rubellus.*

Sediment	Survival (%)			Weight increase (mg/worm)			Reproduction (Number of cocoons)		
	1995	1999	2001	1995	1999	2001	1995	1999	2001
KOBG = reference	95	95	100	-	195	420	65*	25	27
PH cultivated	-	100	100	-	-12	133	-	10	10
PH vegetated upper	-	90	100	-	-42	141	-	16	11
PH vegetated lower	-	80	90	-	-33	93	-	7	6
WEM cultivated	-	90	100	-	29	335	-	10	17
WEM vegetated upper	-	90	100	-	122	301	-	14	19
WEM vegetated lower	-	95	100	-	35	238	-	4	12
GH	95	95	95	-	171	289	59*	26	27
ZZ	95	100	100	-	111	452	54*	25	27

* measured after incubation of 12 instead of 4 weeks (higher reproduction)

Also in 2001 a bioassay with the springtail *Folsomia candida* was used (Table 7.12). This assay shows that in Geul Harbour sediment there is still some toxicity (survival), but we cannot give a specific explanation for it. The springtail is more sensitive in terms of survival than the earthworm.

Table 7.12 Results of the bioassays with *Folsomia candida* (springtail).

Sediment	Survival (%)	Reproduction (number of Juveniles per springtail)
KOBG = reference	100	59
PH cultivated	24 *	16 *
PH vegetated upper	7 *	7 *
PH vegetated lower	0 *	0 *
WEM cultivated	comparable with control[1)]	comparable with control[1)]
WEM vegetated upper	84	48
WEM vegetated lower	7 *	12 *
GH	30 *	34
ZZ	97	57

* *Difference is significant compared to control ($p \leq 0.05$)*

The results of WEM cultivated were comparable with the control. The reproducibility of the control for these samples was, however too low.

Microbiological development

Microbiological activity

Bacterial biomass, growth rate and diversity were only measured in 1999. Results of these measurements are summarized in Table 7.13. The bacterial biomasses in Petroleum Harbour and Wemeldinge sediment are low compared to those in Geul Harbour and Zierikzee sediments. Measured bacterial biomass in cultivated Petroleum Harbour sediment is extremely low and probably an underestimation, because focussing of the microscope is difficult with low bacterial numbers. The growth rates in the cultivated fields and the upper layer of the vegetated fields are high, indicating that management (crop growth, soil tillage) may also have an effect on bacterial growth. In these samples the highest degradation rates of PAHs and mineral oil were also measured (Chapter 4 and 5). The lowest degradation was measured in lower soil layers, for in these layers, bacterial growth is also small. The low growth rates in Geul Harbour and Zierikzee sediments are probably typical for ripened (10 years of landfarming) sediments.

Bacterial activity as measured by dehydrogenases activity (Klimkowicz-Pawlas and Maliszewska-Kordybach, 2003) is influenced by adding of PAHs to clean soils. When PAHs were already present in the soil (aged soil), the effects were much smaller, indicating that the history of the soil or sediment is important. They used adaptation of the present organisms to PAHs as explanation. Their observations showed that results of these types of tests are not always related to the presence of contaminants and other methods for assessment are necessary.

Table 7.13 Bacteria biomass, DNA-synthesis (thymidine), protein synthesis (leucine) and genetic diversity (number of DNA-bands). Values are the mean and standard deviation (SD) is based on 3 measurements. DNA-bands two measurements.

Sediment	Bacteriea(μg C/g)		Thymidine building in (pmol/g.u)		Leucine building in (pmol/g.u)		DNA bands (number)	
	mean	SD	mean	SD	mean	SD	1	2
PH fresh							68	72
WEM fresh							57	56
PH cultivated	6.0	2.5	21.6	2.1	450	18	87	90
PH vegetated upper	43	13	18	0.2	441	52	75	77
PH vegetated lower	59	30	4.6	0.7	129	5	57	55
WEM cultivated	37	5.2	29.6	3.3	457	40	86	85
WEM vegetated upper	16	10	7.6	2.9	191	20	67	69
WEM vegetated lower	14	12	-1.8	0.4	35	5	65	70
GH	103	19	5.3	0.5	81	7	87	82
ZZ	144	21	5.6	1,1	84	7	82	81

Number of genotypes

The observed number of genotypes measured as DNA-fingerprints are in agreement with these observations: low in the original fresh sediments and high in the most developed ones. Not only is the number of genotypes important but also the relative abundance of genotypes as visible in the DNA-fingerprint (Figure 7.6). In the fingerprints of the original sediments, intensive bands are visible, which means that specific genotypes are dominating. Different dominating genotypes are visible, which can be explained by the origin of the sediments: Petroleum Harbour brackish and Wemeldinge saline. The intensive bands fade out during treatment and in the Geul Harbour and Zierikzee sediments, which have been treated for the longest period, no special genotype is dominating.

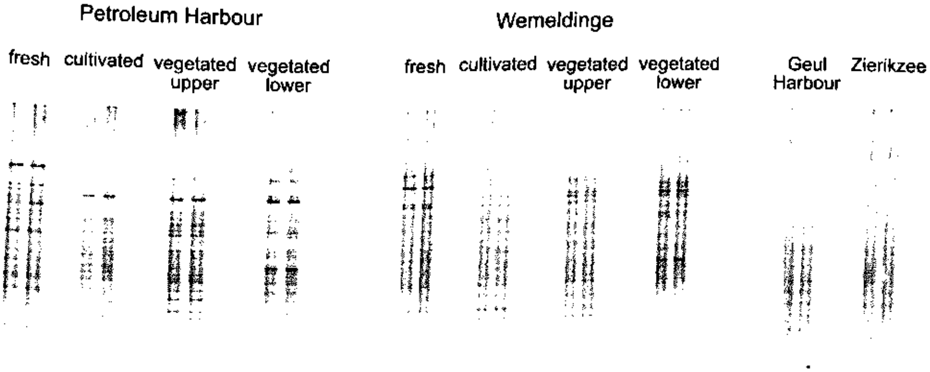

Figure 7.6 DNA- fingerprints of the fresh sediments Petroleum Harbour and Wemeldinge and of sediments treated on the landfarm sampled in 1999.

Nematodes

The higher diversity of biological life in Geul Harbour and Zierikzee sediments is also visible in the diversity of nematodes. In soil ecosystems nematodes belong to various trophic groups: Omnivores and predators are the first to disappear under stress and the last to appear during colonisation (Bouwman and Vangronsveld, 2004). These taxa are hardly present in treated Petroleum Harbour and Wemeldinge sediments (Table 7.14). The diversity of herbivores is largest in treated Geul Harbour and Zierikzee sediments, which is caused by the long period of vegetation, thus stimulating nematodes that feed on plant roots. Presence of roots in the other sediments is responsible for the development of two species of *Paratylenchidae* in very high numbers. In 1999, herbivores are absent in the lower layers of the vegetated landfarm due to the absence of roots. In 2001 roots had entered the lower soil layers, and herbivores were observed.

Combining all the results, Table 7.14 shows that six (results Petroleum Harbour and Wemeldinge of 2001) to ten (results of Geul Harbour and Zierikzee of 1999) years of passive landfarming are necessary to develop a soil with a normal nematode population including omnivores (3 taxa).

Eijsackers (2003) found a quick first colonization by invertebrates (earthworms, isopods and springtails) in PAHs-contaminated fresh water sediment during the first months after deposition. However, further development in number of species and number of individuals per species was hampered in the following year. Probably more time for development is necessary, as has been shown with the observation presented in this ssection.

Table 7.1.4 Numbers of nematodes (feeding types, taxa,) in landfarmed sediments from Kreekraksluizen, determined in 1999 and in 2001. Numbers per 100 g fresh sediment, average of three samples.

Nematodes feeding types taxa	Petroleum Harbour Cultivated		Petroleum Harbour Vegetated Upper layer		Petroleum Harbour Vegetated Lower layer		Wemeldinge Cultivated		Wemeldinge Vegetated Upper layer		Wemeldinge Vegetated Lower layer		Geul Harbour		Zierikzee	
	1999	2001	1999	2001	1999	2001	1999	2001	1999	2001	1999	2001	1999	2001	1999	2001
Total	**13.620**	**3400**	**1270**	**2510**	**1000**	**2860**	**3300**	**2760**	**2830**	**2150**	**1060**	**2700**	**15.730**	**4590**	**4000**	**2750**
Bacterivores	**440**	**150**	**300**	**690**	**990**	**320**	**130**	**780**	**200**	**80**	**1040**	**300**	**210**	**520**	**160**	**130**
Cephalobidae	390	320	260	470	230	200	90	250	160	80	780	200	180	370	50	70
Rhabditidae		70	10	200	150	40	20					30		30	80	20
Diploscapteridae					590											
Monhysteridae	50		10	20	10		20	70	40		250	20	30		30	40
Plectidae		20	20		10	20		20			10	30		60		
Prismatolaimidae						60		440								
Panagrolaimidae		20										20		60		
Teratocephalidae		20														
Herbivores	**13.180**	**2710**	**880**	**1770**		**2540**	**3150**	**1900**	**2620**	**2030**	**10**	**2310**	**14.400**	**3650**	**2130**	**2420**
Paratylenchidae	12.990	760	740	30		130	3150	1620	2620	1130		2160	13.070	1490	690	630
Hoplolaimidae		890	50	20		40		40		40			770	1010	190	40
Dolichodoridae		950		1720		2160		90		360		50	210	270		70
Pratylenchidae		20				60		150				20		150	50	160
Tylenchidae	190	90	90			150				500	10	80	350	730	1200	1520
Fungivores		**240**	**50**	**50**	**10**		**20**	**80**	**10**	**30**	**10**	**30**	**70**	**90**	**190**	**70**
Aphelenchidae		130	10	20			10	40	10	20		30	40	30	140	70
Aphelenchoididae		110	40	30	10		10	40		10	10		30	60	50	
Omnivores/Predators			**40**							**10**		**60**	**1050**	**330**	**1520**	**130**
Diphtherophoridae			40										910	270	1410	130
Dorylaimidae												30	30	30	80	
Mononchidae										10		30	110	30	30	

Contaminants in vegetation

Uptake of PAHs and mineral oil by vegetation is not a problem as explained in Chapter 6. K_{ow} values are high, and PAHs do not pass through cell membranes. Only at high PAH-concentrations (5000 mg/kg d.m), phytotoxicity may occur (Leyval and Binet, 1998). These high concentrations were not present at Kreekraksluizen landfarm and are seldom observed in sediments. Maliszewska-Kordybach and Smreczak (2000) reported that low concentrations of added PAHs (<10 mg/kg sum of fluorene, anthracene, pyrene and chrysene) even stimulate the growth of plants during the early stage of their development. At higher concentrations of the same four PAHs, lowest observed effect concentrations for wheat, oat, maize tomato bean and sunflower were respectively 74; 96; 144; 35; 100 and 111 mg/kg d.m. (average for root length and stem length).

When PAHs in vegetation samples are measured, they are present on vegetation and originate from air, dust or soil particles. They are adsorbed on the leaves or on the roots. Root uptake from soil and translocation of hydrophobic compounds are inefficient processes (Wild and Jones, 1992). PAHs in underground parts come from adsorption of soil particles. Therefore peeling of vegetation such as potatoes and carrots will remove most PAHs. Samsøe-Petersen *et al.* (2002) found that when these crops are grown on contaminated soil, their peelings contain four times at much benzo[a]pyrene than the peeled product. Free hanging fruit (no direct contact with soil) on the same soil did not show an increased PAH-content. By growing vegetation on covered and non-covered contaminated soil, Delchen *et al.* (1999) established that the origin of PAHs was the adhering soil, and active uptake by the roots did not occur. Japenga (2003) showed that the surrounding activities (traffic, industry) are the most important parameter for PAHs content in vegetables and that washing of the vegetables before use is sufficient to remove most of the PAHs. Also Fismes *et al.* (2002) did not find increased concentrations of PAHs in vegetables grown on contaminated soils.

When PAHs are consumed, they originate from air pollution and soil eaten together with the vegetation. These risks for human ingestion are evaluated in risk models like CSOIL (van den Berg *et al.*, 1995; Lijzen, 2001). Similar approaches can be used for ecotoxicological risk of consumption of vegetation growing on a landfarm. Risks will be reduced during treatment due to biodegradation of PAHs and reduction of the available fraction.

Results of the heavy metal measurements in the vegetation (averages of the samples taken in 1999, 2000 and 2001) are given in Table 7.15. Heavy metals were present in concentrations comparable with concentrations normally found in vegetation grown on uncontaminated soil (Wiersma *et al.*, 1986). The low concentrations are in agreement with the relative low concentration in the sediment in combination with the high pH (approx. 7.5). The maximum allowable concentrations for several heavy metals in food for cattle (LAC, 1991) are also given in this table.

Table 7.15 Heavy metals in vegetation grown on the landfarm Kreekraksluizen (average values measured in 1999, 2000 and 2001) and limits for cattle food (in mg/kg d.m.).

Sediment	As	Cd	Cr	Cu	Ni	Pb	Zn
PH cultivated	1.2	0.34	2.3	6.4	3.0	3.3	58
PH vegetated	1.8	0.44	1.2	8.5	3.1	2.5	83
WEM cultivated	1.4	0.24	1.5	4.0	2.1	4.4	27
WEM vegetated	1.1	0.28	1.9	5.1	2.2	4.4	46
GH	1.0	0.59	2.9	10.5	1.8	3.7	60
ZZ	1.2	0.15	1.3	8.5	1.1	2.8	42
Non contaminated food for cattle[1]	<2	<1		<20		<40	<250

[1] LAC, 1991

Plant cover has also an important function in the organic matter cycle in the soil. This is important in managing accumulated contaminants in soil (Eijsackers, 1995). It is difficult to maintain the organic content of the soil in arable land, due to the natural mineralization process by which organic matter is broken down. Extra application of organic matter (for example, application of extra manure) is therefore necessary. Otherwise continued decrease of organic matter will be observed, which may stabilise at a lower organic matter level. Compared to surrounding soils, the organic matter in sediments is usually higher. This is caused by the lower degradation rate of newly developed organic matter (vegetation residues) in the anaerobic sediment. Under aerobic conditions on a landfarm, fast decrease of organic matter content is achieved, as shown in Chapter 4 (decrease from approx. 9% to 5% in 1 year). With the natural vegetation on the landfarm and no harvesting of this vegetation, the organic matter content stabilized at approximately 5%.

7.4 Conclusions

In the perception of most people and as defined in regulations, risks are related to the total concentration of contaminants. In Chapter 3 it has been discussed that the bioavailable fraction of pollutants is probably a better measure for risks. Bioavailability should be combined with the word 'for' and the name of an organism or process. For development of the concept of bioavailability, it is therefore necessary to use methods, such as chemical or biological assays or measures on the biological development of soil or sediment, in addition to measurements of total concentrations. This chapter has shown that different methods can be used to describe the effects of the contaminants present in the sediment. As expected, the decrease of the contaminant concentration has resulted in a decrease of negative effects, as measured with different tests. Although sensitivities for the amount of contaminant differ between the tests, no adverse toxic effects are measured after 2 to 8 years of landfarming, depending on the test.

As long as toxicity using biological methods is measured, it is clear that landfarmed sediment will have a limited use. It becomes more complicated when the effects become comparable with the blank or reference, as found with different assays. Which effect is acceptable, knowing that also slightly different soil properties may influence the measured effect? Should reuse be based on the most sensitive organism that can be used in assays? Answers to these questions are necessary if the assessment of treated sediment is changed from a system based on contaminant concentration to a risk-based system. The results in this chapter as measured on field scale can be used to support this change.

7.4.1 Retention function

The first group of bioassays applied in this chapter were focussed on water that is in direct contact with the sediment or developed soil. This water is in equilibrium with the fast desorbing fraction. The toxicity measured with these assays decreases very rapidly during treatment on a landfarm, and risks are already not measurable after the first year of intensive landfarming. Measuring toxicity in contaminated soil, Van Gestel *et al.* (2001) also observed that most tests in soil extracts (acute tests) did not demonstrate toxicity. A non-toxic concentration in the water phase is in agreement with the results of the leaching test, where non-detectable or low concentrations are measured.

Only in the first year during dewatering, some risks can be present, especially if biodegradation is limited due to insufficient supply of oxygen. After the first fast degradation, contaminants are released by the sediment too slowly to cause toxicity and, after they are released, they will be degraded before they reach the mobile water. Degradation will occur when aerobic conditions are present over the whole layer of sediment. This does not imply that optimum conditions must be present. Under wet conditions, the amount of drainage water will increase and the oxygen concentration will decrease. As long as the oxygen concentration is more than 2%, biodegradation continues (Hurst *et al*, 1996 and 1997). At Kreekraksluizen, all landfarms became aerobic during the whole year as soon as they were dewatered and ripened (see also Chapter 6). All tests on the retention function showed that a landfarm, in which PAHs and mineral oil contaminated sediments are treated, is no threat to the quality of ground water and the receiving surface water.

The observations on Kreekraksluizen suggest another approach to soil protection in landfarms. In a well-functioning landfarm, contaminants will be degraded before they will leach. So in principle a liner, which is often prescribed, is not necessary. A liner may even disturb the proper functioning of a landfarm due to less effective dewatering. It is, however, possible that no biodegradation occurs in a landfarm during dewatering or during temporary anaerobic conditions after a period of intensive rainfall. During these periods, the underlying soil must be able to act as a filter or sink for the contaminants. This will occur if the underlying soil contains enough organic matter (original or added). As rule of thumb, an organic matter content of 3% or more should be used.

7.4.2 Habitat function

Using organisms living in the sediment or the soil that has developed from sediment, toxicity is observed for a longer period. These organisms may take up contaminants before degrading organisms can degrade them. Direct contact of the organisms with the contaminant is an important factor in toxicity. Van Gestel *et al.* (2001) observed toxicity with soil living organisms (chronic tests) in soils where aquatic organisms did not show toxicity.

Toxicity and bioaccumulation can be better explained with the available fraction (chemically measured with Tenax or the fast degradable fraction) than with the total concentration, which supports the importance of the concept of bioavailability as has been described in Chapter 3.

In this research it was necessary to start with bioassays using sediment living organisms, because soil organisms could not survive in the original water-saturated and anoxic sediment. These sediment assays showed a decreasing toxicity during the first years of treatment, but also residual toxicity. Another effect of treatment is that the sediment changed into a soil, which makes application of sediment living organisms not the most logical choice after treatment with landfarming. Therefore the measurement strategy was changed to use of soil-dwelling organisms. Also these organisms showed a decrease in toxicity during treatment, but the sensitivity of different species may differ. When using earthworms, mortality shows a faster decrease of toxicity than reproduction. Earthworms are less sensitive than springtails. The different sensitivities have to been taken into consideration when selecting assays for assessment and setting the final goal for the biological treatment of soils or sediments on landfarms.

Biological methods showed that sediments are developing to a soil with normal functions and biodiversity. It took about 5 years to obtain an ecosystem suitable for colonisation of specific nematode species. Especially for the lower layers in the landfarm, development was slower, because ripening and formation of roots are necessary to stimulate several types of nematode species. In the concept of passive landfarming, this is not a problem, because this is also the time period, which is necessary for degradation of the fast and slow degradable fractions.

No effects were shown in Zierikzee sediment regardless of the tests used. The residual PAHs-concentration was 16 mg/kg d.m. Corrected to the standard soil with 10 % organic matter, this value becomes 29 mg/kg d.m., which is far above the reference value of 1 mg/kg d.m. and just below the intervention value of 40 mg/kg d.m. The residual mineral oil concentration in this sediment was 130 mg/kg d.m (= 230 mg/kg d.m. in a standard soil). This value is also between the reference value and the value for reuse as building material. Clearly there is some freedom of movement between toxicity values derived from regulations and toxicity measured in practice. According to the present regulation, the developed soil could only be used as building material; a risk-based regulation would probably allow a more multifunctional use.

The new reuse value for mineral oil of 2000 mg/kg d.m. (VROM, 2004-b) will make reuse of Petroleum harbour sediment possible after 7 years of landfarming. Some residual toxicity is present in this sediment but this can be acceptable for regulations. The new value will make reuse of Wemeldinge sediment possible even sooner. It takes, however several years for this sediment to develop into a soil with significantly reduced risks. The proposed value of 2000 mg/kg d.m. is therefore too high for Wemeldinge sediment. This high value is not necessary, because a few years of passive landfarming make reuse with reduced risks possible.

8 Effect of spreading of slightly contaminated sediments on agricultural fields

8.1 Introduction

In the Dutch water management system, ditches have an important function in discharge of surplus of water during wet periods and supply of water during dry periods in the growing season in summer. Without maintenance of the system they become silted up by caving in of the bank, sedimentation of particles present in water coming from other areas, and from residuals of vegetation. Vegetation in most ditches is removed yearly, and the sediment in the ditches is dredged every 6-10 years. In the past, spreading of dredged sediments was not a problem, for dredged sediments had a fertilising function and were used to equalise fields. Sediments were spread on the banks of the adjacent agricultural fields in a layer of several to about 20-30 cm (depending on dredging method and density of the sediment). After the sediment was cultivable (dewatered and partly ripened), the farmer spread it further if necessary, ploughed it and grew crops on it (arable land). The sediment was mixed with the underlying soil and became part of the soil in the agricultural field. On pastureland, thinner layers were used, and the grass grew through the dewatered sediment. Mixing of the sediment with the underlying soil on pastureland is a slower process, because the land is not ploughed. Mixing is the result of bioturbation, which is caused by worms, treading of cattle, and also by use of agricultural machinery. Bioturbation is responsible for mixing of the upper 10 cm of pasture land (Boels and Zweers, 2001). Because the sediment was mixed it, became part of the soil. The previous dredged sediment is not recognizable at the application of sediments from the next dredging.

Since we know that sediments contain contaminants such as PAHs and heavy metals, the practise of spreading has become hampered by legal constraints. In an inventory of knowledge and experiences associated with field studies of sediments, Veul *et al.* (2000) concluded that to solve the problem of contaminated rural sediments, we should use active sediment management in combination with a system- and risk approach.

An important part of the pollution in sediments of ditches and watercourses in agricultural regions of the Netherlands is caused by Polycyclic Aromatic Hydrocarbons (PAHs). Kampf (van Puijenbroek and Kampf, 1998) has intensively monitored the regional water system in the northern part of the province of Noord-Holland. Near the cities and industrial areas in the southern part of the province, heavy metals are the dominant contaminants, while in the rural areas to the north; PAHs are the most important contaminants. Most of the sediments are slightly polluted (class 2), regarding to the content of PAHs, as illustrated in Figure 8.1. When the heavy metal concentrations are also low, these sediments can be spread on land.

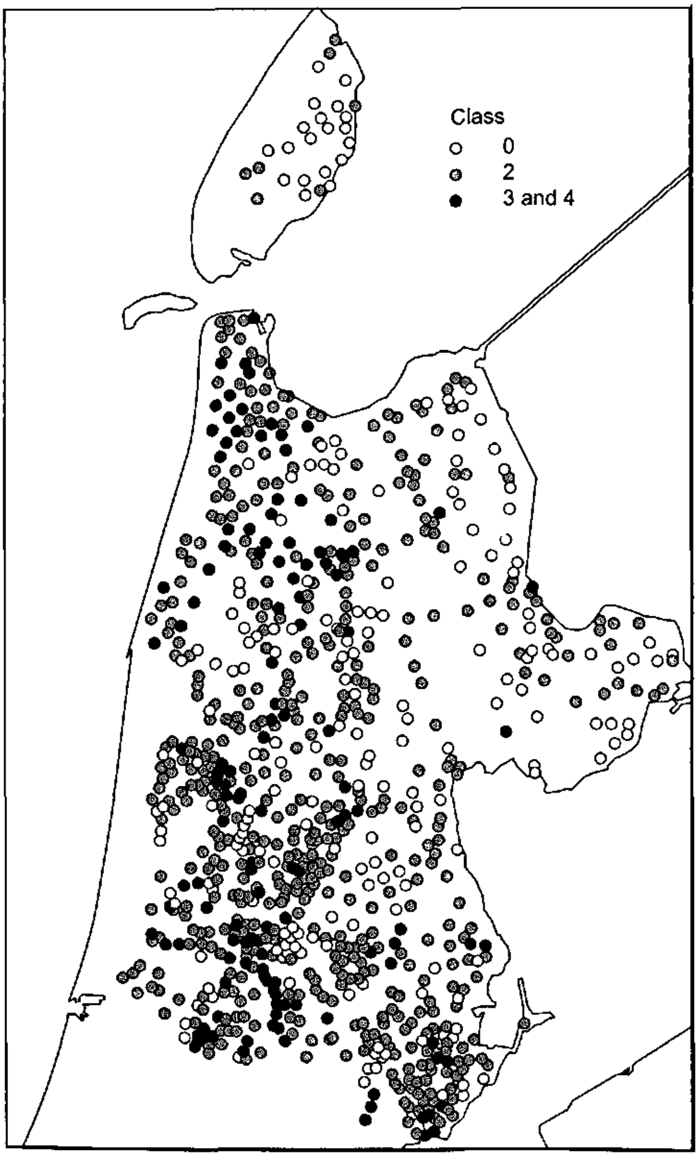

Figure 8.1 PAHs-contamination (classes) in sediment in waterways of the province of Noord-Holland (Van Puijenbroek and Kampf, 1998). Class 3 and 4 = polluted; class 2 = slightly polluted and class 0 and 1 = clean.

In a model study, Huiting *et al.* (1997) showed that spreading of slightly PAHs-contaminated sediments might decrease the soil quality of the receiving soils because of increased concentrations of contaminants. Accumulation in the cultivated soil layer may occur for both heavy metals and PAHs. This theoretical study, based on processes described further, was not validated with field data and more certainty on their conclusions is necessary, especially concerning the role of biodegradation of PAHs on agricultural fields. A study in the UK (Wild *et al.*, 1990) on the effect of amendment of sewage sludge has shown that this activity leaded to an increase of the content of PAHs in the soil. After ending this activity, practised from 1942 till 1960, the concentration of PAHs decreased from 5.5 mg/kg d.m. in 1960 to 2.4 mg/kg d.m. in 1984.

According to Dutch law, it is allowable to spread PAHs-contaminated sediments (class 0 and 1) with values below the reference value of 1 mg/kg d.m (standardised to a soil with 10% organic matter). Sediments containing more than 10 mg/kg d.m. PAHs (also recalculated to 10% organic matter; class 3 and 4) are not allowed to be spread and should be remediated or deposited in a controlled depot. For slightly contaminated sediments with content of PAHs between 1 and 10 mg/kg dm (class 2), spreading was tolerated until the year 2000, assuming that the amount of class 2 sediment will be largely reduced in the future, as the result of clean-up of sources of contaminants (Dutch Parliament, 1993). However, since the amount of class 2 sediments was not drastically reduced, it was necessary to extend the practise of spreading of class 2-sediment in 2000 and again in 2003.

PAHs in the rural area may originate from different sources, as summarised by Kramer *et al.* (1997):

- Diffuse air pollution.
- Traffic.
- Overflow of sewage systems.
- Waste water.
- Creosote sheet pilling.

In a model study, they showed that in spite of source reduction, but based on the sources shown above, large amounts of sediment in the rural area will remain slightly polluted with PAHs (class 2) for the next 50 years.

Knowing that quality improvement of sediment will be achieved slowly and that high amounts of slightly contaminated sediment have to be dredged in the future (AKWA, 2001), new policies are in development to prevent the hampering of dredging of ditches (VROM, 2004). Cleaning of the sediment or depositing in a depot instead of spreading will be very expensive; in addition, it is the question whether this is necessary. Policy should be developed to be able to dredge cost effectively and to spread as much as possible sediment on land without creating unacceptable risks and preventing accumulation on clean agricultural land. The use of bioremediation is a possible strategy to remove PAHs; however, the positive effects of biodegradation are not yet considered in the regulations. The conditions in the top layer of agricultural land are very suitable for biodegradation, because a farmer can create a well-aerated soil system. They can also create optimal soil moisture conditions and hence prevent too dry conditions for biodegradation, because crops will also stop growing in too dry conditions. Moreover, natural processes like earthworm activity (Eijsackers *et al*, 2001) and root turnover (Leigh *et al.*, 2002) stimulate the biodegradation of contaminants.

The concentration of a contaminant in agricultural land is the result of many processes, as illustrated in Figure 8.2. For heavy metals (not discussed in this chapter) all processes except biodegradation, should be considered. For the effect of spreading of PAHs-contaminated sediments, several of these processes are not relevant (as already discussed in previous chapters):

1. Leaching of PAHs to ground or surface water does not occur (see 7.3.1).
2. PAHs are not taken up by vegetation (see 7.3.2).
3. Runoff to the ditch is only a factor when combined with transport of the sediment or soil on which PAHs are adsorbed. Erosion of the walls of the ditch may lead to return of PAHs to the sediment. It is assumed that the sediment, which is formed due to these processes, is spread again on the land during next dredging. This process is therefore not taken into account.
4. The amount of PAHs from other sources was not the subject of this thesis. PAHs are not expected to be present in manure, but are certainly deposited from the air. Anthropogenically-generated PAHs, derived from the combustion of fossil fuels, generally has resulted in an increase of the content of PAHs in soil since 1890 (Jones *et al.*, 1989). The concentrations of PAHs measured in samples taken in 1890 and kept stored until analysis in 1980 were low. The addition of PAHs to agricultural soil with PAHs still takes place. Assuming that all PAHs produced in the Netherlands (462,000 kg in 2002; RIVM, 2004), are deposited again, the average deposition on land is 110 mg/ha/year. If this is mixed in the upper 10 cm of the soil, this gives a yearly increase of the concentration of PAHs of 0.07 mg/kg d.m. The exact amount will depend on the location. It will be higher near roads and urban areas and will be smaller in natural areas. In the 1990s, the emission of PAHs was much higher (i.e. 1726,000 kg in 1990; RIVM.2004).

Factors that are affecting the concentration of PAHs are the amount added by spreading of sediments, the interaction (sorption) with the soil, and biological degradation (5). Consumption of sediment by grazing cattle (6) will not effect the concentration, but has to be considered a risk. PAHs from other sources than sediments can also adsorb on the vegetation growing on the field, also posing risks for grazing cattle. The amount of PAHs adsorbed on vegetation decreases quickly, as shown by Kilian *et al.* (2001), and is caused by volatilization, biodegradation and washing off by rainfall. Half-live of these PAHs are 1-3 days for 2-, 3- and 4 ringed PAHs and up to 9-17 days for the larger ringed PAHs.

Cattle will also consume the spread sediment in combination with the grass. Risks and reduction of risks for cattle should therefore also be based on the availability of PAHs present in sediment for cattle and reduction of the available amount in sediment.

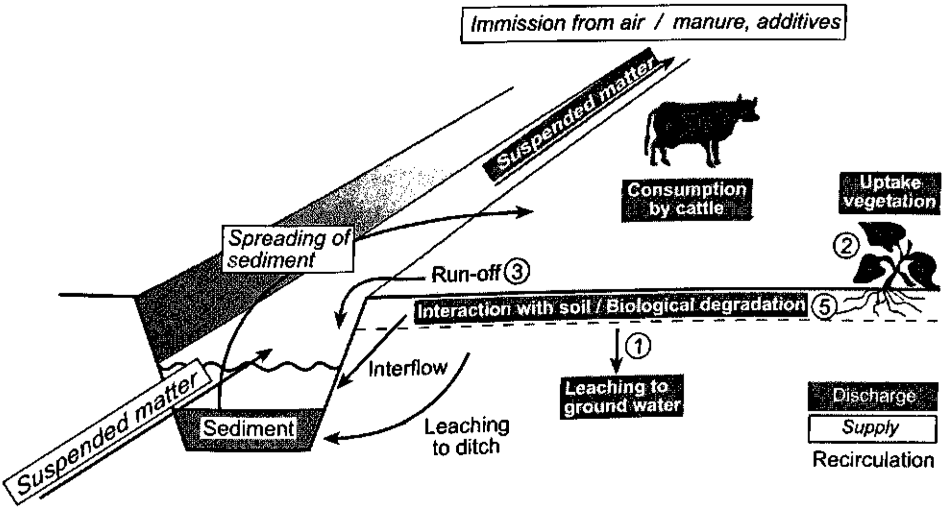

Figure 8.2 Fate of contaminants (input and output) in the ditch/bank system of agricultural land. Numbers are explained in the text.

The objectives of this study were; (1) To investigate if the practise of spreading of the sediment has already lead to unacceptable concentrations in the cultivated soil layer on the banks of the ditches and if the decrease of the PAHs-concentration by natural occurring degradation will reduce the concentrations of the PAHs in the soil to an acceptable level. (2) To investigate if spreading will lead to non-acceptable concentrations of PAHs and non-acceptable risks for the agricultural products and the ecological quality of the agricultural soils. To this end an exploratory examination of fields along the ditches of the Water Board District Goeree-Overflakkee was begun to investigate if deposition of polluted sediment in the past has lead to accumulation of PAHs (van den Toorn *et al.*, 1996 and 1998, Harmsen *et al.*, 1997). To study the impact of natural attenuation, an investigation was also undertaken to determine what happens with PAHs in sediment that was spread out in the usual way, so that normal agricultural practises were simulated. Results of these investigations, in combination with the results discussed in previous chapters, were used to model the accumulation and to predict the quality development of agricultural soils amended with slightly polluted dredged sediment. As mentioned, the presence of heavy metals is not taken into consideration in establishing soil quality.

8.2 Materials and methods

The study has been carried out on the island of Goeree-Overflakkee, situated in the south-west part of the Netherlands (Figure 8.3). The island is composed of polders that have been systematically constructed over the last 950 years. Intensive arable farms and pasture land for cattle dominate this rural area. The dense ditch system on the island is necessary to control the water supply and drainage of the area. The sediment that is formed in these ditches is dredged every 6 years. It is spread on the directly adjacent land, and farmers are responsible for further spreading (if necessary) and cultivation of the land. Comparable with the situation in the agricultural part of Noord-Holland (see 8.1), the sediments on Goeree-Overflakkee are slightly contaminated with PAHs (class 2) and these PAHs are the dominant contaminants.

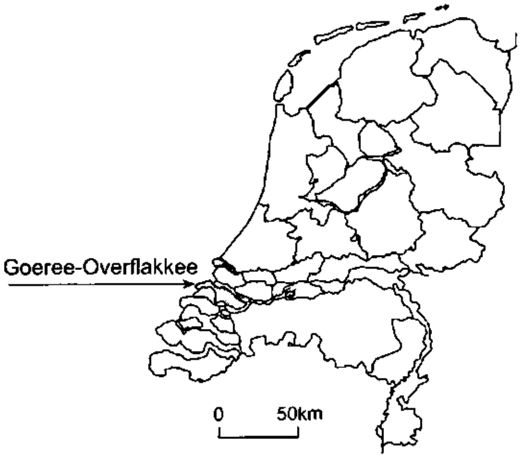

Figure 8.3 The island of Goeree-Overflakkee in the south-west of The Netherlands.

8.2.1 Accumulation of PAHs in the cultivated soil layer

In this part of the study it was examined, if and to what extent, dredging, spreading, and further treatment of the sediment on the bank of the ditches have contributed to increased concentrations of PAHs in the cultivated soil layers. An approach was developed in which the concentrations of PAHs in the cultivated layer on banks were compared with concentrations on the middle of the fields (reference locations) not affected by sediment spreading. The following criteria were used to select the sites:

- Number of times that sediment was spread on the bank.
- Number of years since last dredging.
- Assurance that the dredged sediment was spread on the selected field and not on the field at the other side of the ditch.

- No historical polluting activities on the location (such as waste treatment or old filled up ditches).
- Besides dredging there are no other differences between the bank and the middle of the field used as the reference location.

Sites were selected on which dredged sediment had been spread one to five times and mixed with the original agricultural soil. Accumulation of PAHs in the cultivated layer was studied by comparing the results of PAHs measurements near the ditches (a strip of 3 m along the ditch) with the results of PAHs measurements from samples that were taken in the middle of the field between the ditches. Historical maps of the Water Board and knowledge of the area (Nelemans, personal information) were used to select the sites. Based on the criteria, it was possible to select 25 suitable sites situated in the rural area (Table 8.1). No specific sources of PAHs were present except creosote sheet pilling containing PAHs. Due to the large application of sheet pilling on Goeree-Overflakkee, it was considered as a diffuse source of PAHs. Sediment quality in the investigated area was class 2 and concentrations of PAHs were between 2 and 5 mg/kg d.m. The amounts of sediment spread on the investigated locations were not known. A layer of several cm to 15 cm of dewatered sediment was an indication of the amount of sediment spread.

Table 8.1 Number of sampled locations and their dredging history.

Number of Locations	Number of Dredgings	Years after Last Dredging
3	1	1
1	1	2
4	1	3
4	1	5
4	> 5	1
2	> 5	2
3	>5	3
1	>5	4
3	>5	5

Samples that were analysed in the laboratory were prepared by mixing 12 sub samples (taken with a 4 cm Øgauge auger over a depth of 30 cm) parallel to the ditch in distances ranging from 0-3 m from the ditch. The distance between sub samples was 5m. Reference samples were taken in the same way in the middle of the fields. The samples were homogenised using cryogenic grinding according to ISO 14507 and analysed with HPLC as described in Chapter 4. The data based on measurements of 12 individual PAHs were evaluated using the statistical program GENSTAT 5 version 3.1. PAHs measured were; Fluorene, *Phenanthrene, Anthracene, Fluoranthene,* Pyrene, *Benz[a]anthracene, Chrysene,* Benz[b]fluoranthene, *Benz[k]fluoranthene, Benz[a]pyrene,* *Benzo[g,h,i]perylene* and *Indeno[1,2,3-c,d]pyrene* (see Table 4.2 in Chapter 4). The PAHs in Italic form the Dutch National List. Naphthalene is also included in this list, but not included in this investigation.

8.2.2 Degradation of PAHs on the banks

A field site (location A) in the agricultural area of Goeree-Overflakkee was investigated to determine the fate PAHs in the sediment in the short term (1 year) and in the mid long term (5 years). The field was divided into two experimental fields of 10*20 meter. Before the study was begun, the quality of the original soil of the experimental field and the quality of the sediment was established. The concentration of PAHs in the soil was comparable to the reference locations in the other part of the study. The concentration of PAHs in the sediment was relatively high for ditches on Goeree-Overflakkee, because the dredged ditch was situated near a village and the quality of the sediment was influenced by urban activities. The sediment was transported to the experimental field by truck (12 cargos). On both strips a layer of 20-30 cm of fresh sediment was applied (9-3-1995). The initial condition was determined by sampling every cargo of sediment applied (12 samples).

An investigation was conducted to determine when conditions in the applied sediment were suitable for aerobic degradation processes. This study was accomplished by using oxygen measurements, visual evaluation and measurement of the water content of the sediment. The applied layer of sediment was totally aerobic at the beginning of June 1995 (see results). In order to link our approach to the commonly used method of treatment of dredged sediments on agricultural fields, the dewatered sediment in one test strip was mixed with the original soil (mixing ratio 1 to 1) by ploughing on 8-6-1995, with a second ploughing and use of the rotary cultivator on 2-7-1995. The applied mixing ratio in the ploughed field in this study is low. In agricultural practise, the farmer spreads the dewatered sediment further, and a higher mixing ratio (soil/sediment) is obtained. In this experiment we did not want to have a high dilution of the sediment, in order to be able to measure the amount of PAHs added with the sediment. After 2.5 years (November 1997), the non-ploughed field was also ploughed.

The concentration of PAHs was examinated by sampling in the experimental fields. Both experimental strips were subdivided into 15 plots. For every sampling date, 5 plots were chosen at random in both strips, sampled and analyzed. The fields were sampled intensively in the first year, followed by less frequent sampling in following years.

8.2.3 Prediction of the degradable fractions

As shown in Chapters 3 and 4, it is possible to predict the fast biodegradable fraction of PAHs by applying the Tenax adsorption method. From Chapter 4 it is concluded that it may also be possible to predict the slow degradable fraction using the Tenax-method at 60 °C (Cornelissen *et al.*, 1997). This was investigated using some of the locations described before. In May and October 2003, samples were taken from the banks, middle-field references and from the sediment in the ditches. Four locations were used from the accumulation study (locations 4; 13; 14 and 15 from Table 8.2) and the ditch and field of the degradation study (location A). The Tenax available fractions were measured according to the method described in Chapter 4 using a desorption time of 20 hours and a desorption temperature of 20 °C. The procedure was repeated with fresh Tenax at a temperature of 60 °C, a temperature at which the slow desorbing fraction can also be measured within 20 hours. This fraction was assumed to be representative for the slow degradable fraction. The residual PAHs still present in the sediment were determined as a measure for the very slow degradable fraction. Due to the low concentration in some fractions, the amount of benzo(ghi)perylene could not be measured reliably and is not included in this part of the study. The samples from locations A, 4 and 13 locations were analysed in two-fold, the others in threefold.

8.3 Results and discussion

8.3.1 Accumulation of PAHs in the cultivated soil layer

The results of the PAHs measurement in samples from the banks of the ditches and the reference locations are summarised in Table 8.2, according to the Dutch National List (minus naphthalene) and as distribution between the aromatic ring systems: PAHs having 2 or 3 rings, 4 rings and 5 or 6 rings (see also Table 4.2 in Chapter 4). Table 8.2 shows that all PAHs-concentrations were within the range of 0-2 mg/kg d.m., except the value on the bank of the last location in the table. Further historical research showed that at this location, there was a breakthrough of the dike during the large flooding in February 1953. This dike was covered with an asphalt road, and asphalt from that period contained large amounts of PAHs. Because of this extra source of PAHs, this site should not be part of the selected sites (see criteria in Section 8.2.1), and the measured values were not taken into account in the statistical evaluation.

Table 8.2 Concentrations of PAHs measured on the banks of ditches and the reference locations. PAHs-NL = Dutch National List (minus naphthalene).

Loca-tion	Number of Dredgings	Years last since Dredging	Bank				Reference			
			PAHs-NL (mg/kg d.m.)	Distribution over aromatic rings (%)			PAHs-NL (mg/kg d.m.)	Distribution over aromatic rings (%)		
				2+3	4	5+6		2+3	4	5+6
1	1	1	**0.18**	26	57	18	**0.13**	22	62	16
2	1	1	**0.23**	23	49	28	**0.28**	20	56	24
3	1	1	**0.25**	20	57	22	**0.22**	21	58	22
4	1	2	**0.46**	28	51	22	**0.50**	44	47	08
5	1	3	**0.43**	22	56	23	**0.34**	20	58	23
6	1	3	**0.35**	21	54	24	**0.32**	22	54	24
7	1	3	**0.46**	23	51	26	**0.17**	22	60	18
8	1	3	**0.14**	21	64	15	**0.31**	24	56	20
9	1	5	**0.22**	20	62	19	**0.36**	25	52	24
10	1	5	**0.06**	16	75	08	**0.20**	22	59	19
11	1	5	**0.16**	24	58	18	**0.14**	23	59	18
12	1	5	**1.38**	32	46	22	**0.24**	22	58	19
13	>5	1	**0.54**	25	50	25	**0.49**	24	53	22
14	>5	1	**1.12**	24	49	27	**0.57**	24	51	25
15	>5	1	**1.73**	30	45	25	**1.12**	28	47	25
16	>5	1	**0.20**	19	62	19	**0.18**	18	64	18
17	>5	2	**0.23**	23	55	22	**0.20**	22	58	20
18	>5	2	**0.58**	25	52	23	**0.27**	22	58	20
19	>5	3	**0.48**	27	50	23	**0.39**	27	52	20
20	>5	3	**1.06**	27	48	24	**0.28**	20	58	22
21	>5	3	**0.65**	24	51	25	**0.18**	21	62	17
22	>5	4	**0.27**	21	58	21	**0.15**	21	60	20
23	>5	5	**0.46**	25	51	24	**0.30**	22	57	21
24	>5	5	**1.33**	26	49	26	**0.40**	21	54	25
25	>5	5	**7.67**	37	42	21	**0.63**	27	50	23

The results of the measurements presented in Table 8.2 were statistically analyzed (Table 8.3). Because the values are not normally distributed but fit more closely a log-normal distribution (not uncommonly found with soil parameters), the mean logarithmic concentrations instead of the average values are presented. A significant higher value of the concentration of PAHs in the soil on the banks of the ditches was found, compared to the value at the reference location. This was the case for the sum of the Dutch National List and for the different aromatic ring systems.

Table 8.3 Results of statistical analyses of the comparison of the concentrations of PAHs on the banks of the ditches and on the reference locations. Concentrations of PAHs are presented as the mean-log concentration.

Type of PAHs	Bank of the ditches	Reference locations mean log conc	Statistical results	
	Mean-log conc (mg/kg d.m.)		Significant higher value of PAHs-concentration on banks	Significant decrease of PAHs-concentration between spreadings
PAHs- Dutch National List minus naphthalene	0.40	0.28	yes	no
2+3 ring PAHs	0.17	0.11	yes	no
4 ring PAHs	0.38	0.27	yes	no
5+6 ring PAHs	0.15	0.10	yes	no

Spreading of sediment does not only cause the concentration of PAHs on the banks of the ditches. The reference locations also contain PAHs. The origin of these PAHs could not be related with local sources. It is assumed that these PAHs are from diffuse sources (air pollution). This level of PAHs should also be expected on the banks without spreading of sediment. Comparing the measured values in the sampled layers (upper 30 cm) with values in the sub soil (0.05 mg/kg d.m.) as measured in the soil below the ploughed depth on location A (see 8.2.2), it can be concluded that the reference locations are also influenced by human activities. The values on the reference locations are comparable with values on agricultural sites in Poland and the UK reported by Maliszewska-Kordybach (2000). Comparing the average concentrations on the banks and the reference location from Table 8.3, 70% (0.28 mg/kg d.m.) of the PAHs-load can be allocated to diffuse sources and 30% is caused by the sediment (average for all locations). The concentration of PAHs on the banks with most frequent spreading (locations 13-24 in Table 8.2) doubled during the practise of spreading of sediments.

The time since the last dredging on the different sampled locations varied between 1 and 5 years. No relation could be shown between the concentration of PAHs and the time since last dredging. This is presumably caused by the fast degradation in the first year (see 8.3.2). Because the first samples were taken one year after dredging, the fast initial decrease was missed. The following slow degradation rate, 1 and 5 years after dredging, is small and differences in concentration of PAHs were not significant within the experimental set-up. This is in agreement with the calculations in Chapter 2 and observations in Chapter 4. A residual concentration after 5 years and presence of PAHs in the reference locations show the presence of a very slow degradable fraction as also found on the landfarm (Chapter 4).

The soil on the reference locations contained on average of 3.7% organic matter with a standard deviation of 1.0. For the soil on the banks these data are 4.5 and 1.7 respectively. The increase of organic matter by spreading organic-rich sediment on the banks was not significant. In Dutch legislation, concentrations of PAHs are normalized to a standard soil. For organic contaminants, this means a soil with 10% organic matter. Because the natural organic matter content in soils on Goeree-Overflakkee is low, the normalised concentration of PAH will become higher.

Figure 8.4 gives a frequency distribution of the concentration of PAHs in both the banks and the reference locations, normalized according Dutch regulations to an organic matter content of !0%. In this figure the limiting value for class 2 is also given. It is clear that also on the reference locations some locations are class 2 (38%). On the banks the percentage class 2 is higher, 50%. The reference value for standard soil in the Netherlands for clean soil is 1 mg/kg d.m. The normalized mean log-concentration on the banks of the ditches exceeds this value. Corrected for the organic matter the mean value becomes 1.06 for the bank of the ditch and 0.81 for the reference locations.

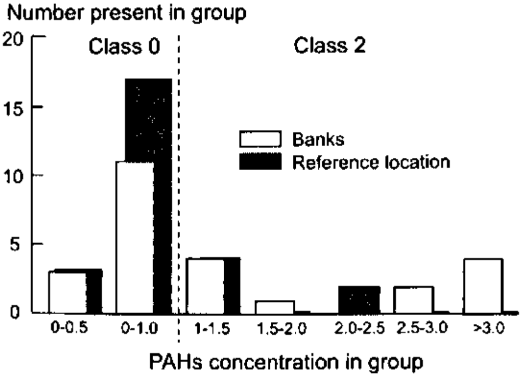

Figure 8.4 Frequency distribution of the PAHs-concentration in soil samples. Concentrations are standardised to 10% organic matter. The Dutch reference value (1 mg/kg d.m.) is indicated with the hatched line. PAHs are presented as the sum of the Dutch National List (minus naphthalene).

8.3.2 Degradation of PAHs on the banks

At the start (March) of the degradation experiment described in 8.2.2, the sediment was complete anaerobic. The water content was about 68%. Due to drainage and (mainly) evaporation of the water, the sediment became aerobic. About 5% of the sediment volume was gas(air)-filled after 45 days (Figure 8.5 A). After 85 days the air-filled volume varied from 5 to 30%, depending on depth (Figure 8.5 B) and the sediment was cultivable. Eighty seven days after spreading, half of the field was ploughed and mixed one to one with the underlying soil, and two different experimental fields were created. After 225 days, between 15 and 30% of the sediment volume of the non.ploughed field was air-filled (Figure 8.4 C), which is close to the air-filled volume in the surrounding fields. In the ploughed soil the air-filled soil volume was slightly higher. This is in agreement with the calculations in Chapter 2, where full aeration is predicted in the upper 25 cm of sediment in the first year after dredging. The measured oxygen content of the sediment/soil gas was 21% or close to this value and was not limiting biodegradation.

A cold and wet spring could have influenced dewatering and degradation of the PAHs (see Chapter 2). Fortunately in 1995 weather conditions were not extreme. Temperatures and precipitation in the period April-October were respectively 9.2; 12.8; 14.5; 20.1; 19.7; 14.2; 12.7 °C and 19; 99; 68; 46; 19; 96; 20 mm (KNMI, 2004).

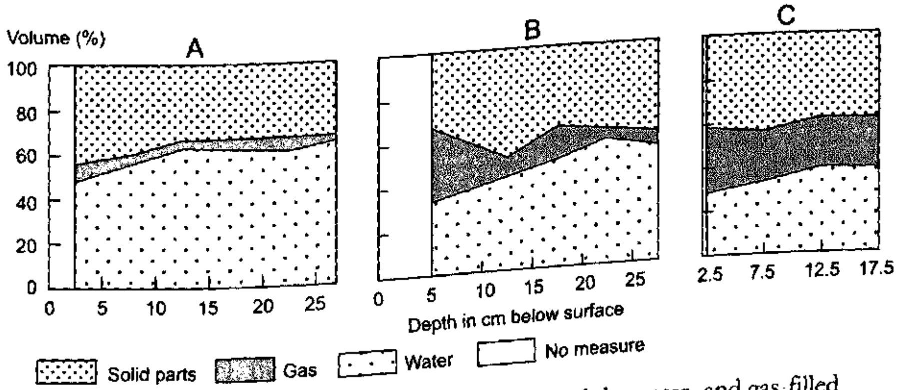

Figure 8.5 Volume fractions of the mineral parts and the water- and gas filled sediment pores in the sediment profile after A: 45 days, B 87 days, C: 225 days.

During the dewatering process in the first months after spreading, the concentration of PAHs decreased in both experimental fields (Figure 8.6). The spread sediment contained a relatively high amount of PAHs (compared to most ditches on Goeree-Overflakkee), but this was favourable in order to obtain a reliable degradation curve. The ploughing and mixing with the underlying soil after 87 days resulted in an additional decrease of the concentration of PAHs by a factor of two (Figure 8.6 B). The concentration of PAHs of the original underlying soil was 0.50 mg/kg d.m. (standard deviation 0.56, n=10). Ploughing of the non ploughed field after 2.5 years also gave a decrease of the measured concentration. In both fields, most of the degradation occurred in the first months (Figure 8.6), followed by a slow continuation of the degradation, as also shown in Chapter 4. After 1.5 years, 68% of the PAHs in the non-ploughed field had disappeared. In the ploughed field the decrease was slightly higher. 80% of the sediment-added PAHs have been degraded. According to results published by Cerniglia and Heitkamp (1989), the observed decrease of concentration of PAHs in both fields was inversely proportional to the number of aromatic rings. In the non-ploughed field, degradation was: 90% for the 2+3 rings, 60 % for the 4 rings and not measurable for the 5+6 rings. In the ploughed field these percentages were respectively, 90%, 70% and 20%. This shows that normal agricultural treatment (ploughing and cultivation) has a positive effect on the degradation of fast degradable PAHs. Presence and activity of earthworms have a positive effect on degradation processes as well (Eijsackers *et al.*, 2001).

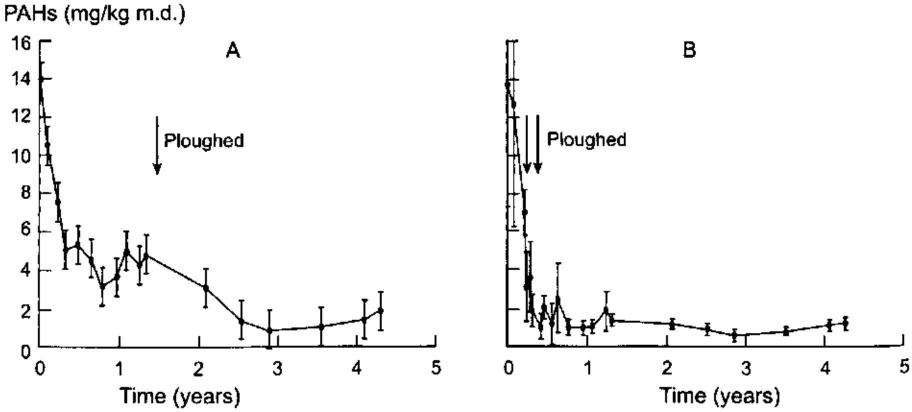

Figure 8.6 The decrease of the PAHs-concentration in sediment on the two experimental fields. A: Non-ploughed field. B: Ploughed after dewatering. PAHs are presented as the sum of the PAHs included in the Dutch National List. For all samplings the 95% confidence interval is presented.

Comparable to the degradation curves presented in Chapter 4, two fractions are visible in Figure 8.6; fast degradation in the first 90 days, followed by slow degradation in subsequent years. Fast degradation in this study was much faster than presented in Chapter 4, which is in agreement with the faster dewatering. The dewatering rate is apparently the time limiting factor again. In the first 90 days, most (>90%) of the fast degradable fraction is degraded, which gives a degradation rate constant of 9.2 y^{-1} or higher. The slow degradation (from 90 days to 2.5 years) in Figure 8.6 A can be fitted with an exponential curve ($c_t = 5.30 \bullet e^{0.21t}$; t in years). Fitting this part of the curve of the ploughed field gave $c_t = 1.62 \bullet e^{0.14t}$. Assuming the validity of the first order degradation model, the actual rate constants for slow degradation of 0.21 and 0.14 y^{-1} are close to the values presented in Chapter 4. It has not been established how long slow degradation will continue and which very slow degradable fraction is left. Using the three-compartment model, the value for the rate constant for slow desorption depends on the size of the very slow degradable fraction. As shown in Chapter 4, a rate constant of 0.33 y^{-1} for slow degradation for use in the three compartment model (see 8.4) seems an appropriate choice.

After 4 years the total amounts degraded in both fields were comparable: 82.5% in the field ploughed after dewatering and 84.5% in the other field. The degradation percentages in both fields of 2+3 rings, 4 rings and 5+6 rings PAHs were also comparable, average values were respectively, 92%, 82% and 51%. Similar to the results in Chapter 4, degradation of 5+6 rings-PAHs is shown if the treatment time is long enough. The distribution over individual PAHs is presented in Figure 8.7. In the first year, the relative concentrations of the lower ring PAHs and especially fluoranthene and pyrene, decrease. After this first year no large changes in composition are seen. Within the normal variation in measurements, the composition did not change anymore, although the total concentration of PAHs still decreased. This shows again that the rate of slow and very slow degradation of PAHs is independent of the number of rings present in the PAH-molecule (see also Chapter 4).

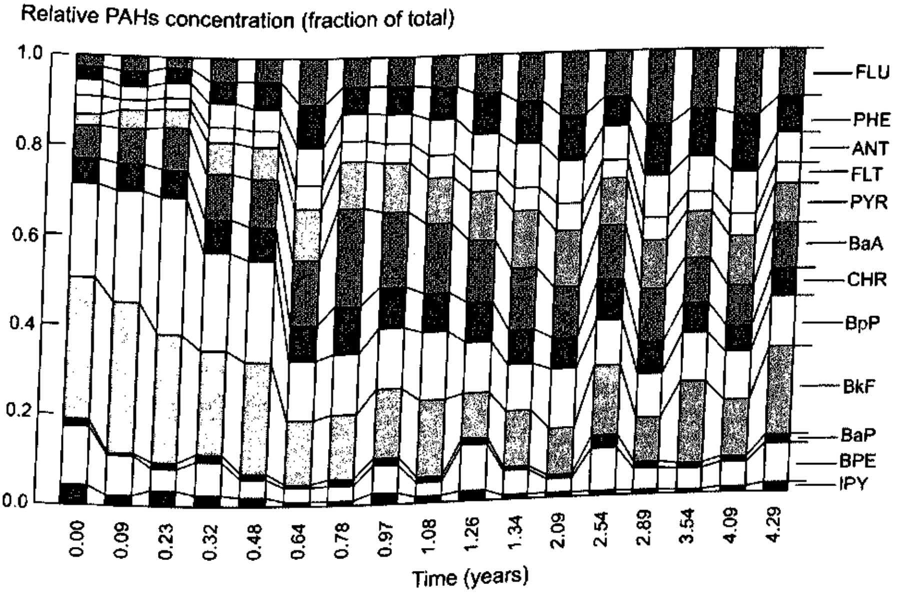

Figure 8.7 Composition of PAHs present in the field not directly ploughed after dewatering.

8.3.3 Prediction of the degradable fractions

Four of the locations given in Table 8.2 (number 4; 13; 14 and 15) and the sediment and soil from location A (discussed in 8.3.2) were used for the measurements of the fast, slow and very slow desorbing fractions of PAHs. These fractions were measured in samples taken from the sediment in the ditch, soil from the bank where sediment has been spread, and soil from the middle of the field as reference. The three desorbing fractions, measured with the Tenax-method (Cornelissen *et al.*, 1997), are presented in Figure 8.8.

The differences between the soil samples taken on the banks and on the reference locations are small. For all locations the fast desorbing fraction is largest in the sediment sampled in the ditch. The size of the fast desorbing fraction in the sediment can be close to the fraction found in the soil samples (locations 4, 14 and 15), but can also be much larger as found on locations 13 and A. On locations 4 and 14, the fast available fraction is low in all samples. On location 15, the fast desorbing fraction is also relatively large in the soil samples. Presumably the highway in the neighbourhood of this location is responsible for fresh and fast degradable PAHs, also on the field. The number of data is too low to make a correlation between probable sources and PAHs present in the sediment, but illustrate the variability obtained after analysing sediments from different locations.

The measured available concentrations based on the sum of 11 individual PAHs, are given in Table 8.4. The sums of different series of PAHs correlate well (Doddema *et al.*, 1998). Therefore, the measured distribution over desorbing fractions can be used as input for the calculations to predict the accumulation (i.e., total concentration expressed as PAHs of the Dutch National List) in soil as a result of spreading of sediments.

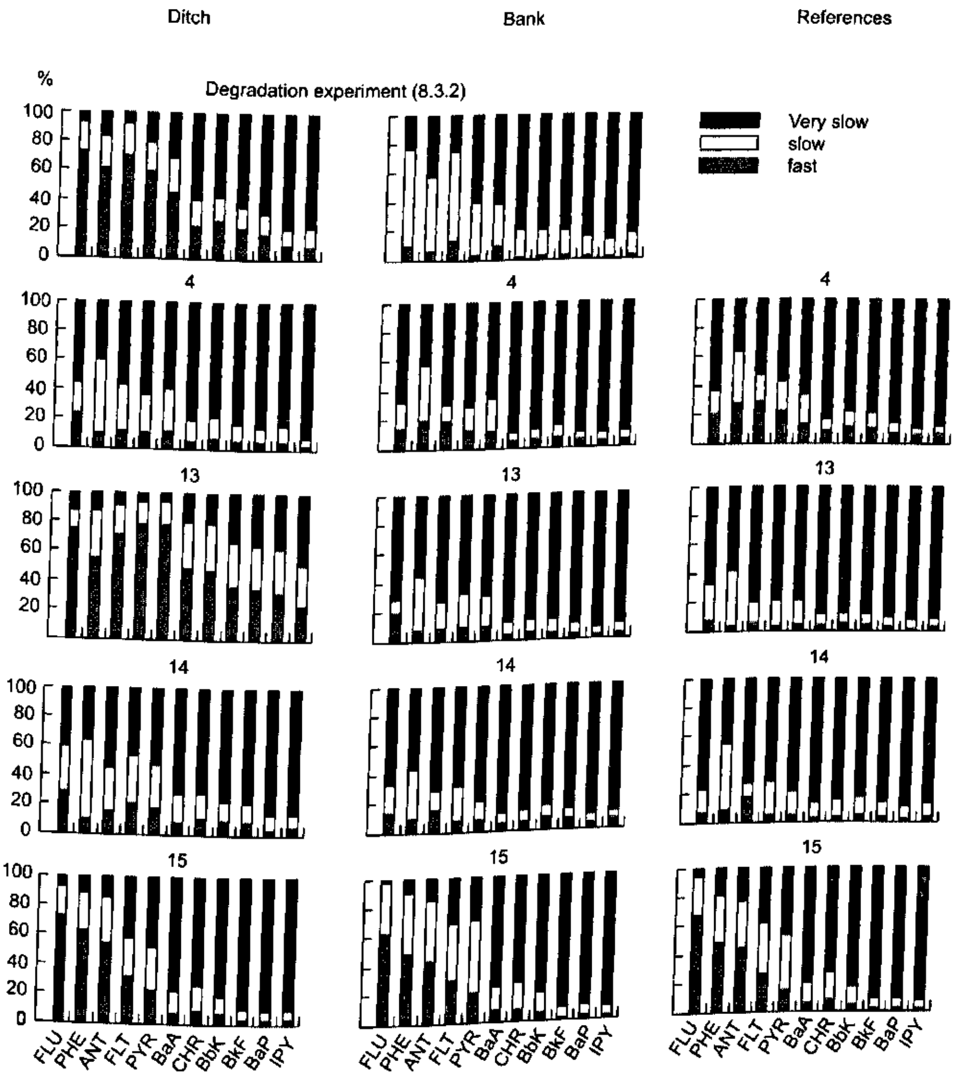

Figure 8.8 Distribution of individual PAHs over the fast, slow and very slow desorbing fractions in samples taken from the ditch, bank and reference on different locations.

Table 8.4 Fast, slow and very slow desorbing fractions of PAHs in different sediments based on the sum of PAHs (sum of measured PAHs). Fraction in % and ()= standard deviation.

Location	Ditch			Bank			Reference		
	fast	slow	very slow	fast	slow	very slow	Fast	slow	very slow
A	47.1 (9.4)	19.1 (1.7)	33.8 (9.4)	4.7 (1.2)	26.4 (1.5)	68.9 (0.3)	-	-	-
4	8.8 (0.2)	22.8 (1.1)	68.4 (1.3)	10.5 (7.0)	13.7 (2.2)	75.8 (9.2)	17.4 (15)	17.4 (2.2)	65.3 (13)
13	71.0 (11)	19.1 (1.6)	10.0 (13)	7.1 (1.0)	16.9 (0.8)	76.0 (0.2)	3.8 (2.6)	14.4 (0.9)	81.7 (1.7)
14	14.5 (2.3)	23.6 (1.3)	61.8 (3.6)	7.4 (0.7)	13.5 (2.3)	79.0 (1.6)	4.6 (1.7)	16.8 (4.6)	78.6 (2.9)
15	41.2 (6.2)	22.0 (8.3)	36.8 (3.1)	36.3 (7.5)	32.9 (4.6)	30.8 (8.2)	31.9 (7.4)	26.0 (2.9)	42.2 (9.6)

8.4 Prediction of PAHs-accumulation and resulting risks on banks of ditches

8.4.1 Three compartment model

For acceptance of the practise of spreading slightly polluted sediments, it is important to know if and to what extent spreading will lead to decreasing soil quality. In relation to PAHs this can be expressed as the future total PAHs-concentration on the banks and the amount of bioavailable PAHs causing risks (see also Chapter 3 and 7). Accumulation on the banks will occur if the supply of PAHs is higher than the amount removed. Biodegradation is the most important process for removal of PAHs and can be described using a three-compartment model (see also previous chapters).

$$\frac{c_t}{c_0} = F_{fast} \cdot e^{-k_{fast} \cdot t} + F_{slow} \cdot e^{-k_{slow} \cdot t} + F_{very\,slow} \cdot e^{-k_{very\,slow} \cdot t}$$

where:

c_t = sediment/soil sorbed amount (mg/kg d.m.) at time t

c_0 = sediment/soil sorbed amount (mg/kg d.m.) at time 0

F_{fast} = fast degrading fraction

F_{slow} = slow degrading fraction

$F_{very\,slow}$ = very slow degrading fraction

k_{fast} = rate constant fast degradation (y^{-1})

k_{slow} = rate constant slow degradation (y^{-1})

$k_{very\,slow}$ = rate constant very slow degradation (y^{-1})

t = time (y)

The degradation rate constants in case of spreading for the fast degradable and slow degradable fractions are respectively 9.2 and 0.33 y^{-1}. For very slow degradation a value of 0.04 y^{-1}, as estimated in Chapter 4, is used. The differences between the three rate constants are large enough to distinguish three fractions. Based on data presented by Wild *et al.* (1990), a slightly lower value of 0.03 y^{-1} can be derived for very slow degradation on agricultural land with PAHs originated from amended sewage sludge. Degradability is an indication that the substance is available and hence, the fast degradable fraction may also cause ecotoxicological risks. This fraction is used to give an estimate of risks after spreading.

8.4.2 Accumulation of PAHs

The accumulation of PAHs is calculated for two typical concentrations of PAHs in sediment spread on land, which are relevant for Goeree-Overflakkee:

- 2 mg/kg d.m, which is representative for most of the sediments on Goeree-Overflakkee.
- 5 mg/kg d.m, the upper limit that is allowed to be spread, assuming an organic matter content of 5% (the upper limit of class 2-sediment is 10 mg/kg d.m. standardised to an organic matter content of 10%).

In the first step of the calculation, the PAHs-concentration of the three degradable fractions resulting from mixing of dredged sediment with the underlying soil is calculated. Different mixing ratios of soil and sediment are possible. This is followed by calculation of the decrease of the concentration due to biodegradation. According to the normal waterway management on Goeree-Overflakkee, dredging is repeated each 6 years, and a new amount of sediment is added. The calculation is repeated until a PAHs-concentration (sum of the three degradable fractions) is obtained that differs less than 1% with previous dredging, just before adding the next amount. Other inputs of PAHs that may affect the PAHs-concentration are ignored in this approach

In the examples presented, it is assumed that the fraction available for fast degradation is low, so that the calculations can be considered as worst case scenarios. Considering the values in Table 8.4, the three biodegradable fractions used are presented in Table 8.5. The quality of the sediment is kept constant during the whole period. The lowest fast available fraction in the sediments, presented in Chapter 4 (Wemeldinge), was also higher (21%) than the value used for this calculations. Further it is assumed that after spreading, arable land is ploughed and a mixing ratio of 1 part of sediment with 4 parts of soil is used. In case of pasture land, sediment is only spread and becomes diluted and mixed with the soil by bioturbation and tread by cattle. The sediment will become mixed with the soil before next spreading and a ratio of 1 of part of sediment with 1 part of soil is assumed. After 6 years, dredged sediment is spread again. Results of the calculations (the different degradable fractions and the sum) are presented in Figure 8.9.

Table 8.5 Input parameters used for calculations of the accumulation of PAHs on banks after spreading of sediments.

	PAHs-concentration (mg/kg d.m.)	Fast degradable fraction (%)	Slow degradable fraction (%)	Very slow degradable fraction (%)
Sediment-1	2	15	25	60
Sediment-2	5	15	25	60
Original soil	1	5	15	80

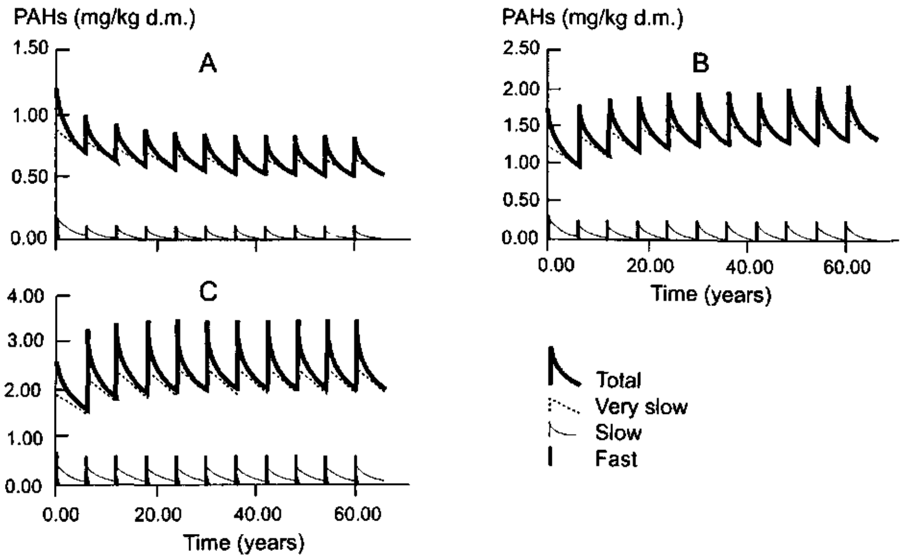

Figure 8.9 Accumulation of PAHs after spreading of sediment on arable and pasture land. A and B: arable land, mixing of 1 part sediment and 4 parts soil (A = sediment-1; B = sediment-2). C: pasture land, mixing 1 part sediment-1 and 1 part soil. Properties of the PAHs in sediment-1 and 2 and soil are given in Table 8.5..

Spreading of sediment with 5 mg/kg d.m leads to accumulation of PAHs resulting in levelling of the concentration of PAHs in the agricultural field after 11 dredgings (60 years). The amount of PAHs added with the sediment equals (within 1%) the amount degraded in the original soil and in the earlier spread sediment. The concentration after 5 spreadings is already close to this value (90% of final value). The doubling of the concentration of PAHs after 5 spreadings, measured on Goeree-Overflakkee (see 8.3.1), can therefore be considered close to the stable end situation. With a different time period between dredging or a change in the quality of sediment, other results will be achieved. For instance, if the sediment quality improves in the future due to a reduction in the source of pollution, a maximum will be reached, followed by a decrease of the concentrations.

The spreading of sediment with 2 mg/kg d.m. also leads to stabilisation of the PAHs level, but at a lower concentration (0.53 mg/kg d.m.) than the original concentration. This is caused by degradation of the PAHs in the original soil and by ignoring the input of PAHs from other sources. If, for example, deposition of PAHs from the air is taken into account, a higher final concentration will be obtained.

From Figure 8.9 it can be concluded that the very slow available fraction is responsible for accumulation. The size of this fraction can, therefore, be used to predict the increase of concentration of PAHs in soil as result of spreading of sediment. Results of the calculations are given in Figure 8.10, where the additional increase of the concentration of PAHs in the soil is presented per mg of added very slow degradable PAHs present in the sediment. In these calculations not only the mixing ratios of soil and sediment as given in Figure 8.9 are used, but also other ratios. Higher mixing ratios are representative for spreading of a thinner layer of sediment.

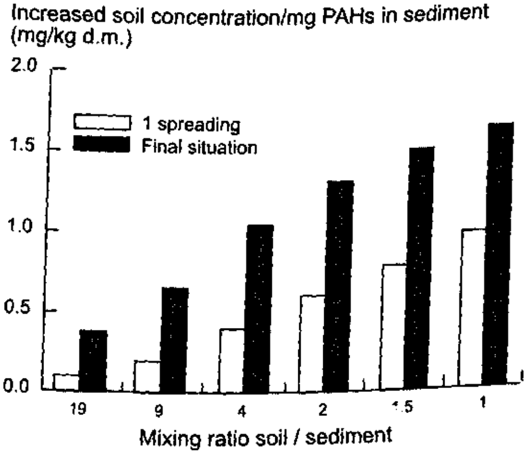

Figure 8.10 Increase of the PAHs-concentration in soil on the bank per mg of very slow degradable PAHs present in the spread sediment, using different mixing ratios of soil with sediment. The increase of concentration is given after 1 spreading and after reaching the final equilibrium situation. Spreading every 6 years.

Figure 8.10 can be used to predict the accumulation of PAHs with different spreading strategies. The obtained values have to be compared with the regulatory standards. The reference level for multifunctional use in The Netherlands is 1 mg/kg d.m. (standard soil with 10% organic matter). Because this level is already close to the background level found on the reference locations (see 8.3.1) there is not much space for further accumulation of PAHs from spread sediment, so the sediment should contain low concentrations of very slow desorbing PAHs and/or should be spread in a thin layer. If the reference value is replaced by a higher, but still risk-less standard, the so-called soil use value for agriculture (van Wezel *et al.*, 2003), more sediment can be spread in future.

If the sediment is spread according to the assumptions in the model, this will lead to an increase of the surface level of the field besides the ditch on which sediment is spread. Farmers equalize the land during cultivation. The result of equalizing will be a concentration gradient from the ditch-bank to the middle of the field. If the deposition strip is close to the ditch, also part of the soil/sediment will wash out the bank to the ditch again (called recirculation in Figure 8.2).

8.4.3 Risks of PAHs

As shown in Chapter 7, risks of PAHs are related to the bioavailable fraction expressed as available for fast desorption or fast degradation. The fast available fraction decreases as a result of degradation by micro-organisms. This activity of micro-organisms is high in summer and low in winter (see Chapter 2). Dredging is mostly done in autumn and winter and due to the low temperature in this period, fast available PAHs will be present until the following spring, when micro-organisms become active again.

In the approach used, it is assumed that all fast desorbing PAHs are available and may cause risks. The fast available fraction reduces with a first order decrease and a rate constant of 9.2 y^{-1}, starting in April, which is sufficient to degrade 99% of the fast available fraction during the summer period (May-September). The results of the calculations for the application of sediment are presented in Figure 8.11 for different amounts of fast available PAHs present in the sediment. Based on laboratory experiments with added and thus available PAHs, the Dutch reference value (upper limit for clean soil) is set at 1 mg/kg d.m. Assuming that a fast available amount of more than 1 mg/kg d.m. present in the sediment may cause risks, these risks will be present as long as degradation does not occur (during the winter period) after application of sediments containing this available amount. In the winter period the sediment will dewater and risks will quickly reduce as soon as degradation starts in the first months of the summer period. The figure represents the risks on pasture land in the first year after dredging. On pasture land, mixing is only the result of bioturbation which is a slow process. It is not known yet if the digestive system of grazing cattle influences the availability of PAHs and if for cattle, the slow and very slow available fraction has to be taken into account. On arable land, mixing with underlying soil by cultivation will reduce the risks of the original sediment as a result of the reduction in concentrations.

Uptake of PAHs by plants is not a problem, as described already in Chapter 6 and 7. If PAHs are present on vegetation, they originate from adsorbed sediment or soil particles or from other sources (air pollution). As mentioned in the introduction, the rate of disappearance, reported by Kilian *et al.* (2001) for PAHs present on vegetation, is much higher. After a few weeks, risks of these PAHs will be small compared to risks of PAHs present in sediment.

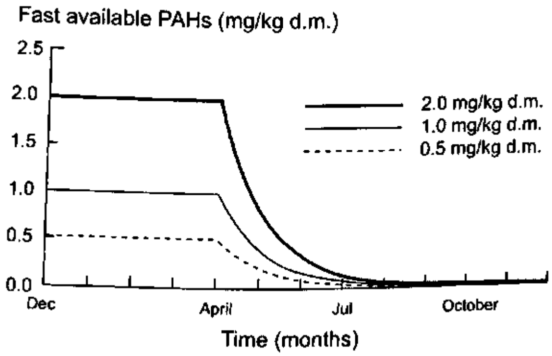

Figure 8.11 Decrease of the for fast degradation available fraction of PAHs on agricultural land after spreading. Original concentrations fast available as indicated in the figure.

In next autumn, degradation will slow or cease due to the lower temperatures and wet conditions (see Chapter 2). In autumn and winter, a new fast for degradation available fraction is formed from the slow available fraction. Because the sediment was already dewatered in previous winter, a desorption rate of 0.33 y^{-1} has to be used. During the second winter half year, 16% of fraction available for slow desorption, still present in autumn, becomes available for fast desorption. This fraction will be responsible for risk effects; degradation of this fraction starts again in April. The fast available fraction in the second spring will be small compared to this fraction in the first spring. Therefore only the fast available during the first year after spreading has been calculated.

8.5 Conclusions

PAHs present in sediment spread on agricultural land are subject to biodegradation. Although the concentration in sediment that are spread is lower than in sediments treated on a landfarm, the same three degradable fractions as presented for more strongly polluted sediments in Chapter 4 can be distinguished: fast degradable, slow degradable and very slow degradable. Because the thickness of the layer spread is smaller than in a landfarm, dewatering on agricultural land goes faster. In addition, the conditions for degradation on agricultural land are good: optimal aeration, presence of vegetation and application of nutrients to stimulate activity. A faster degradation of the fast available fraction is therefore measured. The degradation rate of the slow degradable fraction is comparable with the rate measured on a landfarm (see Chapter 4).

When comparing soil on which sediment is applied and a reference situation without sediment, an increase of the concentrations of PAHs is observed. After 5 spreadings, a doubling of the concentration of PAHs was seen. Calculating the concentrations of PAHs in the future, it was shown that after 5 spreadings, 90% of the final concentration is achieved. In this final situation, the amount of PAHs added in the sediment equals the amount degraded on the bank and is achieved after 11 spreadings (=60 Years). On Goeree-Overflakkee, ditches are dredged every 6 years. The calculations also show that the very slow degradable fraction is responsible for the accumulation.

The fast degradable (available) fraction is responsible for the amount of PAHs causing risks. A higher risk concentration (> 1mg/kg d.m. PAHs of the Dutch National List) can be present until about 1 month after biodegradation has begun (spreading of sediment with a fast available fraction >2 mg/kg d.m and no mixing with soil). In Dutch conditions, this means that after spreading in autumn, a period with higher risks can be present until spring. Temperatures from April onwards will be sufficient for degradation. Highest risks will be present on pastureland, because mixing will only be the result of bioturbation, and cattle can be in contact with the original sediment. This risk should be prevented by not allowing cattle to graze on strips where sediment has been spread until May or June following dredging. With lower available concentration in the sediment and mixing with soil, the period of risk can be smaller. If the available fraction is larger or if an extra safety factor is used, which leads to a lower target value, the period of risk will be longer.

In general, a large fast available fraction will lead to short-term risks and low long-term risks (accumulation). If the fast available fraction is small and the very slow available fraction is large, the short-term risks will be low and accumulation will occur, which will lead to concentrations above the background level. The risks of the accumulated PAHs will be small, but unlimited accumulation will not be acceptable, when this leads to values above the limit value for highly polluted soil. Which value is acceptable in relation to risks is subject of further studies (van Wezel *et al.*, 2003; Posthuma *et al.*, 2004).

In the calculations to predict the accumulation on the banks, the three degradable fractions (fast, slow and very slow) were derived from measurements with the Tenax-method at 20 and 60 °C. Although variations in measurements between different sediments were relatively large, this method seems promising and can be used in combination with the calculations to predict the effect (accumulation and risks) of spreading PAHs-containing sediment on agricultural land.

9 Evaluation and discussion of landfarming of contaminated sediments

9.1 Introduction

Polycyclic Aromatic Hydrocarbons (PAHs) and mineral oil can be removed from polluted sediments using bioremediation methods under aerobic conditions. Landfarming is one of these bioremediation methods. It is subject of this thesis and different aspects have been described in previous chapters:

1. Development of landfarming in relation to increasing knowledge and changing regulations.
2. Theoretical description of the most important processes in landfarming of sediments; activity of biodegrading organisms, transport of contaminants in sediment and limitations regarding microbial availability of oxygen in landfarmed sediments.
3. Bioavailability of contaminants as an important factor and methods to predict the bioavailable fraction for degradation and environmental risks.
4. Degradation of PAHs and recognition of slow and very slow degradable fractions of PAHs.
5. Degradation of mineral oil in landfarmed sediment.
6. Possibilities to increase the rate of degradation and thereby decrease the treatment time.
7. Environmental risks in and around a landfarm.
8. Effects of spreading of dredged sediments on agricultural land as a special application of landfarming.

An important conclusion in this study is that biodegradation of contaminants in landfarmed sediments can be subdivided into three steps; (1) fast degradation, (2) slow degradation and (3) very slow degradation (Figure 9.1). This is based on theoretical considerations, laboratory experiments and long term (12 years) field experiments on the experimental landfarm Kreekraksluizen. Contaminants in dredged sediments are present in three forms regarding rate of biodegradation: fast, slow, and very slow based on bioavailability for degrading organisms. In addition to bioavailability, the presence of oxygen is important. Because dredged sediments are anaerobic, time is required for dewatering to occur that allows oxygen transport into sediment pores, and this oxygenation step is an important factor for the first fast step in biodegradation.

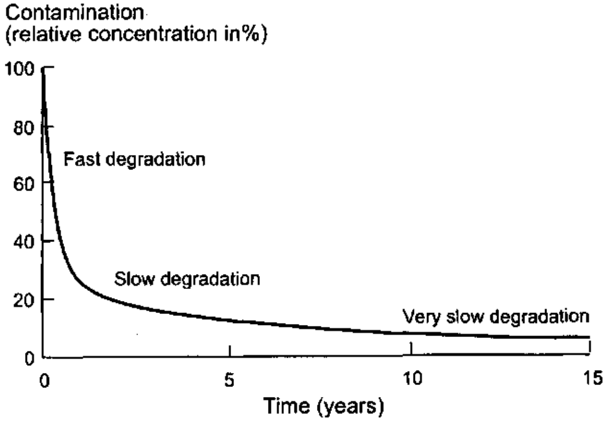

Figure 9.1 Idealised biodegradation curve of contaminants in landfarmed sediment.

In bioremediation studies, most effort has been put into improvement of technologies in order to achieve both lower residual concentrations and shorter treatment times. Considering only the fraction available for fast degradation of the contaminant, shorter treatment times can be achieved. The effect on the slow and very slow available fraction is very small. This thesis identifies and considers slow and very slow degradable fractions, and demonstrates that it is possible to achieve improved remediation results, especially on a landfarm. The necessary longer treatment time required for treatment necessitates a minimisation of active management activities (input of energy and labour) in order to reduce the costs of treatment.

For landfarming of sediments, it is necessary to dewater the dredged sediment in order to obtain the proper aerobic conditions for biodegradation. Biodegradation will occur when conditions assure biological activity (neutral pH, organic matter for a rich soil life and nutrients for microbiological processes). This was the case in the investigated sediments. In this thesis the following ways of landfarming have been distinguished:

- **Intensive landfarming:** processes are optimised using active management activities to reduce contaminants to residual concentrations as quickly as possible.
- **Passive landfarming** with minimal management activities where rapid bioremediation is not necessary, and can be used for reducing residual concentrations.

The preferred way of landfarming depends on the target values to be achieved, the time available for achieving the target values, and the area of land that can be used for treatment. Application of both ways of landfarming will change treated sediments into reusable soils.

In the first part of this chapter the most important aspects of previous chapters are brought together in order to describe the possibilities of landfarming, especially if long treatment times are possible. The most important time determining factors and the possibilities and necessity of optimisation of the application of these process factors for landfarming are discussed. This resulted in presentation of a mathematical model to predict the treatment time in passive landfarming based on reduction of the contaminant concentration. Landfarming is an effective treatment for sediments contaminated with PAHs or mineral oil. If these are the only contaminants as in the experiments described, landfarming of sediments will lead to reusable or clean soil.

Methods to overcome the effects of heavy metals present in sediment are described in the second part of this chapter. The presence of heavy metals in sediments may interfere in reuse of the sediment, thereby limiting the application of landfarming. Although heavy metals were not the subject of the research described in this thesis, it should be an omission not to include this in the final discussion.

The third part of this chapter discusses possible applications of landfarming. Due to the low availability of part of the contaminants for biodegradation, long treatment times will often be necessary. This means use of an area for a long period, which will be possible only, if this occurs in combination with beneficial land use. Existing applications and a look ahead at possible applications of passive landfarming in combination with beneficial use and biodegradation in more natural systems are described.

9.2 Biodegradation of PAHs and mineral oil in sediments on landfarms

9.2.1 Bioavailability

Treatment of the sediment should lower environmental risks. In regulations, this is set by target values to be reached. However, total concentrations of contaminants, as found in the field, cannot be correlated with risks as measured in ecotoxicological tests. It is the fraction of the contaminant bioavailable for organisms involved that should be considered. The bioavailable fraction is not the same for all organisms. In soil and sediments, it is therefore necessary to distinguish risks and the decrease of risks for the water compartment (retention function) and the decrease of risks for organisms living in soil or sediment (habitat function).

The concept of bioavailability is used in different parts of this thesis. It has been shown that bioavailability is not a fixed concept with a single meaning for all users of the concept. Different definitions exist depending on the background of the user. This is not a problem as, long as bioavailability is used in connection with a biological process or effect. If this connection is not made it will stay a confusing concept. In this thesis bioavailability is further used in combination with biodegradation of PAHs and mineral oil. Bioavailable for degrading organisms is defined as:

> *The amount of PAHs and mineral oil that can be transported (by diffusion or physical change of the adsorption site) to a site with a degrading micro-organism in a defined time period and that can enter the bio-influenced zone of this organism.*

This bioavailable amount will be biodegraded under aerobic conditions in that period, providing there are no other limiting conditions for degradation. This definition is a conceptual one that can be used for all bioremediation techniques. Time may vary from days to weeks in a bioreactor and from years to decades in a more natural remediation system. With an infinite time the bioavailable fraction will theoretically equal the total amount of contaminants. Therefore an operational definition of bioavailability is necessary. Within the context of an operational definition of bioavailability, which has been used in this thesis, the bioavailable fraction is defined as:

> *The amount that is degraded aerobically on a landfarm in one year, under Dutch climate conditions.*

Chemical methods can be used as a tool to predict biodegradation. Results of chemical methods cannot be used to define the bioavailable fraction but can only be used as an estimate of the bioavailable fraction. For the bioavailability of PAHs the Tenax-method that was used was shown to give good predictions of biodegradation.
There is no chemical tool available yet to predict the bioavailability of mineral oil as defined above. Mineral oil is a complex mixture of components with different features and is present in different phases. Mineral oil is strongly associated with the organic matter in sediments.

9.2.2 Time determining steps in landfarming

Aeration

The first step in landfarming of sediment is dewatering, followed by ripening to obtain an aerobic and stable soil structure. The presence of air filled pores enable the supply of oxygen necessary for aerobic microbiological degradation processes. Dewatering and ripening give further physical changes to the sediment, which can be described as compaction and shrinking. The sediment becomes a soil with cracks and soil aggregates. The distribution and sizes of cracks and aggregates depends on the soil water potential. In the upper layer of a landfarm and especially if vegetation is growing this potential is high, resulting in a distribution such that all soil aggregates will be aerated. At greater depths and closer to the ground water table the soil aggregates are larger and diffusion of oxygen into the aggregates becomes more difficult. It is shown that the structure in dewatered and ripened sediment is less compact (lower bulk density and larger air filled volume) compared to a soil with the same properties (clay and organic matter content). This is a positive effect for landfarming because the larger air filled volume enables better supply of oxygen. The soil aggregates will only become aerobic (oxygen present) if the amount of oxygen diffusing into the aggregate is larger than the amount consumed by micro-organisms for degradation of organic matter.

Using a model that describes the aeration process (Chapter 2), it is shown that in a landfarm with a layer of 1 meter of dewatered sediment, the most effective way to create an aerobic structure is to conduct intensive treatment in the first year or to use vegetation with a deep root system. Measures that are not effective include increasing the temperature and increasing the oxygen concentration in the cracks. On the experimental landfarm Kreekraksluizen, dewatering using tillage and using vegetation was compared for a layer of 1 meter depth (Chapter 6). Tillage gave an aerobic layer within one year that was also calculated with the model. When using vegetation, about three years were necessary to obtain vegetation covering the whole field and to achieve a fully aerobic layer. Salt present in the sediments was responsible for the slow development of the vegetation. An excess of rainfall was necessary to leach the salt present. A faster development of vegetation will also give faster aeration.

Dewatering occurs when more water leaves the landfarm by leaching, surface run off and evaporation than is supplied by rainfall and capillary rise. Under the Dutch climate conditions (excess evaporation in summer, but surplus of rain over the whole year), it is shown that stimulation of surface run off is necessary when the sediment is not intensively cultivated. Because the permeability of dredged sediments for water is small, the amount discharged by drainage will be small. An extra under pressure (50 mbar) under the sediment did not increase the leaching (Chapter 6). Without surface run off to discharge the rainfall, the dewatering in summer will be undone in winter.

In a passive landfarm, sediment is not cultivated and vegetation has an important role. In the dewatered and ripened sediment, leaching and capillary rise are influenced by the water table and as a result the air filled volume becomes smaller deeper down in the direction of the water table. This effect depends on soil type, is larger with increasing organic matter and clay content, and is discussed in Chapter 2. In summer, the sediment is aerated in the rooted layer, because the evaporation from this layer is high. Below this layer the air filled pore volume first drops slowly and becomes small after reaching a critical depth. At the water table all pores are filled with water and therefore the water table in a landfarm should be low. In Figure 9.2 the air filled pore volume is presented as calculated for the Petroleum Harbour sediment (26% clay and 9.1% organic matter). The figure represents the situation in summer, when evaporation exceeds precipitation and the high temperature stimulates biodegradation. In this example, roots are present to a depth of 20 cm. Other depths of roots and sediments with other soil characteristics will give other profiles.

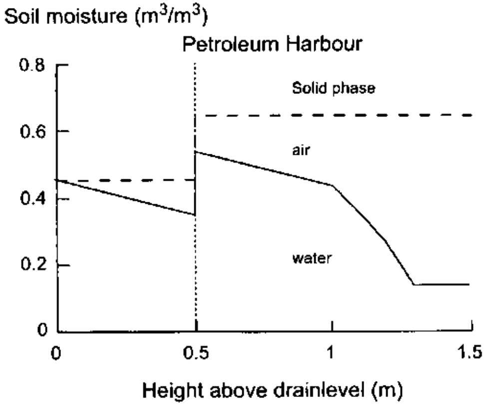

Figure 9.2 Pore volume distribution as calculated for Petroleum Harbour sediment in summer.

On the landfarm and in sediment spread on agricultural land, it has been shown that the fast degradable fraction is degraded during dewatering. The dewatering rate is therefore the time determining step for the degradation of the fast available fraction. Dewatering using vegetation is fast enough so that it is not the limiting factor for the slow degradable fraction. The overall result is that the degradation rate of both fast and slow degradable fractions is the same for stimulated (intensive) dewatering using tillage and passive dewatering using vegetation. Therefore, if it is necessary to degrade (part of) the slow available fraction, intensive landfarming is not effective, because passive landfarming will give the same results.

Desorption

Degradation can be described as desorption of the contaminants from an adsorption site and diffusion to a place with an active micro-organism. Desorption can, like degradation on a landfarm (see further in this section), be described as a sum of first order processes. The fast desorbing fraction of PAHs (measured with desorption experiments) can be used to predict the fast degradable fraction, showing that desorption is an important process in degradation of PAHs. It is shown in Chapter 2 that the desorption rate constant (first order rate process) is proportional to the square of the moisture content in aggregates, becomes smaller if the pore volume reduces and is reversed proportional to the square of the radius of the aggregate size.

Desorption is therefore much slower in dewatered and ripened sediment treated in an aerobic (unsaturated) landfarm with large aggregates then to desorption as measured in most laboratory studies. Desorption constants measured in the laboratory of saturated and stirred sediments (this study, and also referenced studies) are often derived from measurements in slurry systems, which are (over)saturated with water and well mixed, giving small aggregates and large pore volumes. These measured desorption rate constants can be used to predict degradation rates in slurry systems, but are not directly usable to predict the degradation rate in a landfarm. It is necessary to take into account the moisture content and the radius of the soil aggregate. Using the derived expression for the rate constant (Chapter 2) it is shown that it is necessary to decrease the aggregate size to less than 1 mm in order to increase the desorption rate for slow desorption. This cannot be achieved by normal agricultural treatment. Root development and activity of earthworms may decrease aggregate sizes, but it will require a lengthy period of time to realise this for all sediment treated. Root development and earthworms will have a positive effect on degradation in passive landfarming.

With the slow degradation rates measured, the sediment cannot be considered as a material with a constant composition. Not only contaminants are degraded, but also the organic matter will be attacked by micro-organisms. Rate coefficients for the decrease of organic matter are reported (Rijtema *et al.*, 1999) and are comparable with the rates for slow and especially very slow degradation of PAHs and mineral oil. In a passive landfarm residuals of vegetation also give new organic matter. In the long term experiments on Kreekraksluizen it was not foreseen to establish the influence of the dynamics of organic matter on the degradation of PAHs and mineral oil and therefore dynamics of organic matter and the consequences for the fate of contaminants should be subject for further study.

Active micro-organisms

Presence of micro-organisms to degrade PAHs and mineral oil is not a problem in a landfarm. If the proper degrading organisms are not present in large numbers in the sediment, an active degrading population will develop during dewatering and ripening of the sediment. The time necessary for dewatering is large compared to a possible acclimation time of micro-organisms. In the research presented in Chapters 4, 5 and 8 no acclimation time could be observed.

Adding of active micro-organisms and especially addition of fungi has been suggested by others to increase the degradation. These aerobic organisms can only be added in dewatered sediments, because they will not be active and probably will not survive in the original anaerobic sediment. After dewatering, most of the fast degradable fraction is already removed by the populations of micro-organisms that developed under natural conditions. To degrade this fraction, added organisms are not

The activity of organisms will be higher too, but this is shown not to be a relevant factor during passive landfarming of sediments. Other processes, oxygen supply during fast degradation and desorption during slow and very slow degradation, are the limiting factors. The most important factors are: dewatering rate, diffusion and probably degradation of organic matter. Under cold conditions the activity of micro-organisms may become a limiting factor.

9.2.3 Prediction of the treatment time

Slow degradation or the presence of a residual concentration of the contaminant after the treatment is said to be caused by a small bioavailable fraction. The presence of a residual concentration after landfarming of sediment means that the contaminants left in the sediment are not available for the degrading organisms within the treatment time used and treatment method. Extending the treatment time will lead to a lower residual concentration, because more of the contaminant will become available. Degradation rate constants for the three degradable fractions are presented and when the sizes of the fractions are known, a three-compartment model can predict the degradation curve. Because the sum of the fractions is 1, only two of the three fractions have to be measured (within the accuracy of the methods).

In this thesis the Tenax-method (Cornelissen, 1997) has been used to measure the different available fractions. The fast desorbing fraction measured with this method correlates with the amount of PAHs degraded in one year. If the amount of measured fast desorbing PAHs is about 10% or lower, slow or very slow degradation occurs (see Chapter 4). Applying the Tenax-method at 60 °C gives an estimate for the slow degradable fraction. This is shown for sediments spread on agricultural fields (Chapter 8). Validation for sediments applied on landfarms is still necessary and may be application of the method at even higher temperatures may give an estimate of the very slow degradable fraction.

In Figure 9.3 the predicted degradation curve is constructed for 3 sediments with an assumed distribution of the three fractions (Figure 9.3). Comparing sediment 1 and 2, the influence of the slow degradable fraction is shown. Especially in the first years the degradation rate in sediment 1 is higher. If for instance a target value of 20% of the original concentration is accepted, sediment 1 could be cleaned in half of the time necessary for the second sediment. If a low residual concentration is compulsory a longer treatment time is necessary. After about 10 years both sediments will follow the same curve, because only the very slow available fraction remains (same size in both sediments). The residual concentration is set by the size of the very slow degradable fraction in combination with the treatment time. Sediment 3 contains a large very slow degradable fraction. More than 10 years are needed to reach the target of 20% of the original concentration. A further slow decrease is shown, but for sediments with a large slow degradable fraction, very long treatments will be necessary to reach lower target values. Biodegradation on a landfarm may take a long time, but continued degradation does occur, which results in decreases in risk and opportunities for other uses of the land following remediation.

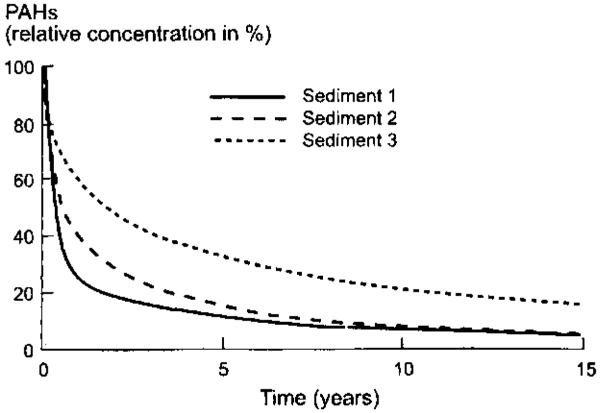

Figure 9.3 Predicted degradation curves calculated with the three compartment model (see previous section). Assumed distribution over different degradable fractions (%):

	Fast	Slow	Very slow
Sediment 1	70	20	10
Sediment 2	50	40	10
Sediment 3	30	40	30

Using the experimental data of the degradation of mineral oil, it was not possible to recognize a very slow degradable fraction. This fraction was not present or too small to measure. Probably the degradation of mineral oil can be described with two fractions; fast and slow. For this two-compartment model, the degradation rate constant for fast degradation is the same as presented for PAHs in Table 9.1, and for slow degradation a value of 0.17 y^{-1} should be used.

The three-compartment model can also be used to predict the accumulation of PAHs after spreading of slightly contaminated dredged sediments on agricultural fields. On the island of Goeree-Overflakkee ditches are dredged every 6 years and the dredged sediment is spread on the banks of the ditches. Using this practice it is shown that a constant PAHs concentration on the bank is obtained after 11 dredgings (60 years). After 5 dredgings, already 90% of the final value is attained. Compared to reference locations (only diffuse PAHs loading from the air) the measured doubling of the PAHs concentrations on the banks after 5 dredgings will be a good estimate of the effect of spreading of sediment on Goeree-Overflakkee.

9.2.4 Risks during landfarming

For environmental regulations the contaminant concentration is often used for conducting risk assessment. With landfarming, and especially with passive landfarming, the concentrations of contaminants decrease slowly. This makes landfarming, in spite of its simplicity and low cost, a method, which is difficult to accept by the public. It is necessary to present to the public data on real risks, not only of the cleaned sediment, but also of the risks during landfarming. It is assumed that landfarms are not open for the public (especially in the first years after starting) and that the target values to be reached are risk less values for human beings. Therefore, only environmental risks are considered, which can be distinguished in risks for the retention function and risks for the habitat function. The retention function is related to the ability to adsorb contaminants to prevent them from mobilizing or from being translocated into the food chain. The habitat function is the ability to serve as a habitat for organisms in or on the soil. Different tests can be used to indicate the risks for both functions.

Tests or assays for the retention function are based on measurements in the water phase, not having direct contact with the solid part of the sediment of soil. In the first year of landfarming these tests still showed effects, but the effects quickly reduced. It is shown that a landfarm on which PAHs and mineral oil are treated is not a threat for the quality of groundwater and the receiving surface water. Leaching is not a risk during landfarming of PAHs and mineral oil contaminated sediments. As soon as aerobic conditions are obtained, contaminants available for leaching will be degraded before they can leach. Instead of a liner, soil with natural organic matter or added organic matter can be used as soil protection. Organic matter is an effective adsorbent for organic contaminants. This way of soil protection is also positive for dewatering, because a lower water table is possible without liner.

Risks for the habitat function are shown to be present for a longer period. Organisms used in assays for the habitat function are in physical contact with the solid parts of the sediment. During passive landfarming it was necessary to replace the sediment assays by terrestrial assays. All applied assays have shown that, together with a decrease of the contaminant concentration and especially the bioavailable concentration, risks reduces during passive landfarming. Nevertheless, several years are needed to have no measurable risks anymore or to build up a normal soil fauna. Although concentrations of the contaminants were not low enough to allow multifunctional use (no risks based on concentration), no measured risks are present at Kreekraksluizen after 10 years of passive landfarming.

9.3 Heavy metals as limiting factor for treatment of sediments on landfarms

PAHs and mineral oil are not always the only contaminants in sediment. Heavy metals may also be present. Bioremediation does not have an effect on the heavy metal concentration and in the presence of heavy metals these metals can cause a toxic end product. To reduce the effects of heavy metals, additional treatments need to be combined with the landfarm activities in order to reduce the amounts and risks of PAHs and mineral oil. Possibilities are described in the following sections.

9.3.1 Phytoextraction

Plants may accumulate heavy metals from soils, sediments and water. The extent of this accumulation depends on the plant species and soil/sediment and contaminant type. For many plant species this accumulation process is passive. The removal of heavy metals from soils in agricultural crops will very gradually reduce soil heavy metal levels in the absence of fresh inputs. However, for some plants accumulation of metals appears to be an active process possibly related to a tolerance mechanism for their survival on contaminated sites and these plants are referred to as 'hyper accumulators' to distinguish the nature of their metal accumulation from the passive accumulation that is general for plants and typically does not lead to such high leaf concentrations of metals (Japenga, 1999). Agricultural crops and crops easily growing on landfarmed sediments are typically not hyper accumulators, although some clones may have higher metal uptakes than others. There has been much recent research on the ability of so called short rotation coppice (SRC) species to take up heavy metals, and thus decontaminate land affected by elevated concentrations of these contaminants. An overview is given in (Paulson *et al.*, 2003) and the technique is open to discussion on its sustainability and risk management grounds as well as practicability.

The use of chelates to enhance the availability for plant uptake can be of help to remove metals from the soil, but care should be taken to avoid losses by leaching. In non-controlled systems such as free draining areas, leaching losses are actually exceeding the uptake of plants by far. In controlled systems such as concrete basins where leaching water can be collected, a combination of crop growth of metal-tolerant plants and wastewater treatment can result in an effective clean-up of the soil (Römkens *et al.*, 2001). Under natural conditions as will be applied for passive landfarming, however, the use of synthetic chelates most likely will lead to enhanced leaching and groundwater pollution. Careful design and management of chelate-enhanced phytoextraction treatments at the field scale, therefore, seems necessary. But still a long time will be necessary for treatment. It is doubtful whether this can be realised in a passive landfarming-like system, because non-predictable climate conditions could be responsible for leaching. Chelate enhanced phytoextraction can be a proper solution to clean metal polluted sediment only in areas where evaporation exceeds precipitation.

On Kreekraksluizen the heavy metal content in the vegetation has been measured (Cadmium 0.34 mg/kg d.m. and zinc 53 mg/kg d.m., see also Chapter 7). Based on this concentrations, and a dry matter production of 10 tons/ha, it will be possible to extract yearly 0.0034 kg/ha Cd and 0.53 kg/ha Zn. Assuming that the same amount will be extracted every year, a dry density of the soil of 1000 kg/m^3 and original Cd- and Zn-concentrations of respectively 2.1 and 210 mg/kg d.m. the necessary treatment time can be calculated. 1500 years (Cd) and 1000 years (Zn) will be necessary to reduce the heavy metal content in the upper intensively rooted 50 cm with 50%. If the uptake is a percentage of the amount present, the treatment time will be larger. Using willow and slightly more polluted sediment, Vervaeke *et al.* (2003) could extract 0.04 kg Cd/ha/y and 1.7 kg Zn/ha/y. If the amount in the vegetation is low as shown above, very long treatment times will be necessary and phytoextraction will be wishful thinking.

9.3.2 Immobilisation

Sediments are anaerobic and in most cases the heavy metals are strongly bounded as sulphide or carbonate. During landfarming the sediment becomes aerobic and sulphides are oxidised, by which the solubility of the heavy metals increases. Moreover, the pH can decrease if the buffer capacity of the sediment is low. As a result, the availability for soil living organisms, leaching and plant uptake may become too large. If the passive landfarm is not designed to treat the surplus of water and to harvest the vegetation for a long period, then additional measures may be necessary. These can be distinguished in measures taken in the aerobic landfarm to decrease the availability or to return again to anaerobic conditions in which immobile sulphides are formed. Because heavy metals are not removed, immobilization should lead to a sustainable system.

Immobilisation under aerobic conditions

In a landfarm, aerobic conditions are stimulated in order to increase the biodegradation of organic contaminants. If heavy metals are present, their availability has to be decreased by adding an immobilising agent. Landfarming can be extended to treatment of sediment contaminated with both organic contaminants and heavy metals by using the results of research into immobilisation of heavy metals in soils. An immobilising agent should have the following properties (Osté, 2001): 1) High metal binding capacity; 2) Selective metal binding; 3) Durable; 4) No negative site effects; and 5) Inexpensive. Groups of materials having several of these properties are: lime, alumino silicates, Fe/Al/Mn-(hydr)oxides and material rich in organic matter.

The effect of the pH has found to be the most important factor. Fortunately the pH in dredged sediments is often higher than the pH in soil of the same area, so availability will be low when landfarming the sediment is initiated. If the buffer capacity of the sediment is high by presence of lime, oxidation of sulphide present in the sediment will not lead to a drop of the pH. This has been observed in the investigated sediment on Kreekraksluizen. If the buffer capacity is low and sulphides are present, adding of an immobilizing agent will be necessary to compensate for the pH-drop. The pH in Petroleum Harbour- and Wemeldinge sediment was high enough to prevent high uptake by crops and leaching (see Chapter 7). There was also no transport observed from the most upper layer to lower layers (Harmsen *et al.*, 2002a).

Natural immobilization

Heavy metals are not available for organisms, when they are present as insoluble salts like sulphides, which are produced under anaerobic conditions. This process can be stimulated when the proper preconditions are present (Harmsen *et al.*, 2002b). These conditions are: anaerobic sulphate reducing conditions, supply of sulphate and presence of iron as regulator of the sulphide chemistry. Translated to sustainable conditions natural immobilization means:

- A high groundwater table as present in a seepage area. Diffusion of oxygen in a water saturated system is much slower (as explained in Chapter 2).
- A consumer of oxygen to maintain the sulphate reducing conditions. Presence of organic matter content will ensure this condition.
- Supply of sulphate and iron to precipitate the heavy metals. In a seepage area this means presence of these compounds in the groundwater.

Natural immobilization will not occur in a landfarm, because aerobic conditions are present. The proper conditions can be created under the landfarm by making a filter in the water-saturated zone, which prevents heavy metals to leach to the ground- or surface water. This is also a long-term process, because leaching is a very slow process in landfarmed sediment especially at the high pH present in a lot of sediments. In the Petroleum Harbour and Wemeldinge sediment treated on Kreekraksluizen It was not possible to recognize transfer of heavy metals to lower layers in the period 1995-2001. Another way of natural immobilization is transferring the landfarmed sediment, in which PAHs and mineral oil are degraded, to a location where the proper conditions for natural immobilization exist.

9.4 Potential applications of landfarming

Intensive landfarming can be considered as a bioremediation technology for which a special site is constructed to clean dredged sediments. After remediation, preferably within one year, the cleaned sediment can be reused. Such a site is characterized by a high transit of sediments and the only function of the site will be cleaning of sediments. The capacity of the site can be increased by stimulation of dewatering or by increasing of the layer thickness. Only the fast degrading fraction will be removed.

As described in this thesis, passive landfarming is appropriate for bioremediation of polluted sediments, especially for the removal of the slow and very slow degradable fractions. When using passive landfarming, only measures are taken to maintain the proper conditions for biodegradation. Most important of these conditions is the presence of oxygen over the full layer applied. In contradiction to intensive landfarming no extra cultivation is applied. Passive landfarming is very close to normal agricultural practice, not only in relation to the treatment of the soil, but also due to the function of vegetation in maintaining the proper conditions for biodegradation.

The long treatment time of passive landfarming will put a claim on the use of land, which will not be a problem if enough land is available. This will, however, be a problem in densely populated area. Most of the contaminated sediments will be present in densely populated areas. It will therefore be necessary to combine passive landfarming with another way of beneficial land use. In this section a few applications are described. Besides the spreading of sediments on agricultural fields, these applications have not been extensively described in previous chapters. They have been discussed in different working groups, some are already applied, and others are in development. They can be considered as an application of the results and a looking forward to the future.

It is not always necessary to clean the sediment on a special site. The necessary conditions for bioremediation are also present under natural (field) conditions. If a site is under development or will provide another function in the future, then the time necessary to develop this function can be used to clean the sediment. If sediments are applied, the site can be closed for the public during development. As soon as the site will be open for the public, used for agricultural purposes or fulfil a role in nature development, absence of the risks related with the contaminants has to be necessary (risk-based approach). As shown in this thesis, this is possible with PAHs and mineral oil contaminated sediments.

9.4.1 Spreading of sediment on agricultural fields

In the Netherlands a large amount of sediments is dredged in the rural area. Originally all of these sediments were spread on adjacent agricultural fields. Since we know that sediments can be contaminated, the practice of spreading is regulated. As shown in Chapter 8, biodegradation is stimulated on agricultural fields and is responsible for removal of organic contaminants. Spreading should not lead to decrease of the quality of the agricultural land. With low concentrations of PAHs (PAHs Dutch National List till approximately 10 mg/kg d.m.) the accumulation is acceptable and the available concentration will be low enough not to cause risks.

9.4.2 Use for nature development

Natural sites in development can be used for biodegradation PAHs and mineral oil in dredged sediments. In wet conditions as present in a lot of Dutch natural sites degradation will not occur. Under these conditions only natural immobilisation of heavy metals will be stimulated. If both aerobic and anaerobic conditions are present, the area is probably suitable for treatment of sediments polluted with both organic contaminants and heavy metals. Dry parts or frequently dry parts can be used to degrade PAHs and mineral oil and the continuous wet places for immobilization of heavy metals and to accumulate heavy metals leaching from aerobic parts. Wetlands are examples of those sites and these areas can also be constructed. Sediments can have a role in development of such a site. Instead of spending the money to only cleaning, it can be used for the development of a wetland. Applying sediment on the proper places will lead to a soil or sediment and will reduce the risks of the contaminants. The time to develop the site is used for cleaning of the sediments.

9.4.3 Use in constructions

If sediments are clean enough, they can be used as building material. In 2004 the reuse target values for PAHs and mineral oil in sediments were respectively 40 and 2000 mg/kg d.m. Reuse as building material results mostly in use inside of the construction (mostly elevations like dikes and noise walls, landfills and foundations of roads) and consequently the conditions for biodegradation will be compromised. (not enough supply of oxygen). Use of PAHs or mineral oil contaminated sediment on top of the construction (aerobic part) will lead to continuing degradation and on the long term achieving of a soil not providing any risks. This in contradiction with the use in the construction, where risks will always be present.

An example is the application of sediment to make dikes higher. Rising of the sea level will make it necessary to make safer dikes in the forth coming decades. This will ask for a high supply of soil. If the activities will be started now, sediments can be used as cover and will give a saving on other sources. The sediment will develop in a structured and clean soil and will help to make saver dikes. Other examples are verges of roads, noise walls and landscape development.

9.4.4 PAHs in the floodplains

Large amounts of polluted sediments are present in the floodplains of the large rivers in the Netherlands. Sedimentation in the floodplains occurs during every high water period. Starting at the industrial revolution in the second half of the 19th century the sediment became polluted and the pollution was at its maximum in the middle of last century. At the moment the quality of the sediment is much better, due to environmental measures taken in the countries within the river basin. PAHs are important contaminants present in the sediment, but not the only contaminants; heavy metals and chlorinated compounds can also be present. Even in the most contaminated period the water in the rivers contained oxygen and the rivers acted as bioreactors. Consequently the fast degradable fraction of the PAHs was degraded during transport and the sediment mainly contained slow and very slow degradable PAHs.

An example of a sediment profile is given in Figure 9.4 (Wieggers, 1996; Harmsen, 1997). This figure also contains data of surface samples take between 1958 and 1981 and stored under dry conditions (which prevented further degradation) and measured in 1988 (Japenga, 1990). The figure presents the 6 Borneff PAHs (fluoranthene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, benzo[g,h,i]perylene and indeno[1,2,3-cd]pyrene), which were measured in both investigations. A similar profile was measured in the sediment of Lake Michigan where the maximum amount of PAHs was sedimented around 1942 (Schneider *et al.*, 2001). Assuming that the value measured in the surface sample of 1958 represents the highest concentration present in the fresh sediment, it is possible to calculate the degradation rate constant. From the two profiles presented in Figure 9.4, a first order degradation constant of 0.016 y^{-1} or a half-life time of 43 years can be calculated. This shows that the PAHs in the floodplains are mostly present in the very slow degradable fraction. This is confirmed by Smreczak and Harmsen (2001) using the Tenax method, between 5 and 8% of the PAHs were available in the fast desorbing fraction, and with this percentage very slow degradation can be expected (as concluded in Chapter 4).

Due to presence of coal particles in sediment from the river Rhine it is possible that also an extreme slow degradable fraction has to be considered in this sediment (see also 4.4.1). The chemical binding of PAHs to coal is stronger (Jonker, 2004) and about 25% of the PAHs in Rhine sediment from the most polluted period, is present in coal particles (Harmsen, non published data). The coal particles originate from the washing of coals in coalmining areas downstream of the river Rhine. They coloured the sediment more black and can be used to locate the more contaminated layers sedimented since the beginning of the industrial revolution (Mulder, 1989).

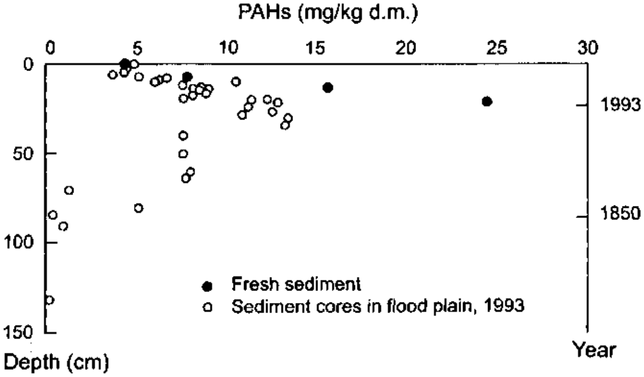

Figure 9.4 Profile of PAHs (6 Borneff) contamination in the floodplain of the river Rhine.

For safety reasons, becoming actually after the extreme water levels in 1995 and 1996, it became necessary to create space for the river. This can be created by additional channels in the floodplains which provide extra discharge capacity during high water levels. Because the sediment is polluted, it has to be relocated in the area and otherwise it has to be cleaned or stored in a confined disposal, which is not a realistic approach given the large amount of polluted sediment present? Relocation can be realised by using pits in the area created in the past for the extraction of sand and gravel. In this case the sediment will be stored under anaerobic conditions and no further degradation can be expected. It would be better to relocate sediments with PAHs as main contaminants on higher location in the floodplains, where aerobic conditions can be achieved and biodegradation will occur (Faber *et al.*, 2001).

Regarding risks it will not be necessary to remove all PAHs present in the sediment. The quality of the surface of the floodplains is set by the quality of new sedimentation. Currently the fresh sediment (Figure 9.4) contains approximately 4 mg/kg d.m. PAHs (6 Borneff). Based on the degradation rate for very slow degradation in this thesis, this PAHs-concentration and even lower will be achieved in the more polluted sediment already present in the floodplains. The PAHs-concentration in freshly added sediment will also decrease. Without new sediment the quality of the floodplains will continuously improve. Because the river will always supply new sediment, the future quality of the floodplains will not be set by historical pollution, but by the quality of fresh sediment.

9.4.5 Biomass production using Short Rotation Coppice

Biomass production on land is seen as an opportunity to provide non-fossil fuel energy feedstock. The Netherlands aims to achieve 10% sustainable energy in 2020 (385 petajoules), of this 25 petajoules has to come from biomass production (Novem, 2002). Fast growing species of willow and poplar are grown and harvested by coppicing on a regular cycle to produce useable wood biomass for a range of applications, including bio energy. The tree is cut back to just above ground level after the first year of growth causing many new shoots to develop. Harvesting involves the cutting and removal of these shoots at regular (normally 2-5 year) intervals. This practice is called Short Rotation Coppice (SRC) and maximises the social and economic as well as the environmental benefits of biomass production on marginal land (Paulson *et al.*, 2003). This has a beneficial effect on the economics and in particular cash flow thus making the economics of both the restoration and the development of a commercial crop highly favourable.

In the Netherlands SRC is seen as an opportunity for the re-use and remediation of sediments. Oostwaardhoeve is an experimental farm in the north/west of the Netherlands on which this is practised (Breteler *et al.*, 2001). Cultivation of willows as biomass for energy production has been studied on this farm since 1993. From 1996 this cultivation has been combined with the remediation (landfarming) of polluted sediments. In treating sediments SRC-crops have an extra benefit, because they have a positive effect on dewatering (Chapter 6). During the treatment the quality of the sediment improves due to biodegradation of PAHs and mineral oil.

The proper application of sediments on a hectare scale requires a thorough macro-filtration of the sediment, so that objects that may be encountered in the sediments removed from the bottom of waterways, like bicycles, car wheels, etc. are removed before the sediment is transported to the landfarm. Application of sediment in an even layer on the land requires experience and technical skill to tune the pumping equipment to the acceptable variation of quality and quantity of the applied sediment. It appeared easier (Harmsen *et al.*, 1999) to apply sediments to an existing willow crop than to establish a new crop on a layer of fresh sediment (Figure 9.5). On the other hand, the existing crop presented a barrier towards the even distribution of sediment. Approximately 1.0 m of sediment could be applied, which layer became, in agreement with the calculations in Chapter 2, a fully aerated layer. Because a willow crop will be started for at least 10 to 20 years, this period is also available to clean the sediments to the extent that the remaining material fulfils the legal requirements for reuse (Breteler *et al.*, 2001). The crops are harvested in the winter, during periods that it is possible to drive on the land (dry or frosty conditions). The harvested willow stems are dried completely on the field to increase the yield of energy. They are not cut, because cut willow is easily composted during drying, which reduces the benefit for energy supply (Gigler, 2000).

Figure 9.5 Sediment in SRC for remediation (Oostwaardhoeve), one year after application to an existing willow crop.

The bioremediation part of the combination on Oostwaardhoeve works. The economic success, however, depends on the profits from the harvest biomass. In spite of the Dutch policy to stimulate the production of energy from renewable sources (Bergsma, 2002), the profit of the biomass grown on Oostwaardhoeve is low (Harmsen *et al.*, 2002-c). The management of Oostwaardhoeve is therefore looking for possibilities to increase the beneficial use of the sites where sediment is treated to include landscape development, recreation and use of other crops (Goedbloed, 2004 personal communication; de Poel *et al.*, 2004).

Sediments as cover of a landfill

The development of a landfill is a time consuming process. Several decades often pass before the area will be available again for another destination. This time can be used to bioremediate sediments. The sediment to be cleaned should be used to cover the landfill and not as waste inside the landfill. On top of the landfill bioremediation will take place during further development of the landfill, with beneficial use as clean soil as final goal.

A special case has been developed for use in Nizhnekamsk a town near the Kama River in Tatarstan, part of the Russian Federation (Harmsen and Sims, 2002). The problem involves contaminated industrial sludge. The properties of sludge are comparable to the properties of organic rich sediment. Also sludge has to be dewatered before degradation starts. In Nizhnekamsk a large chemical factory wants to clean a large amount of heavily polluted sludge to prevent pollution of the Kama River ecosystem. Although the sludge is very polluted (almost 50% of the sludge consists of mineral oil and different chemicals) micro-organisms are present and can be activated (Nikitina *et al*, 2003). Effective biodegradaion has been demonstrated in pilot experiments (Galukhin *et al.*, 2002). In the treated material toxicity has decreased significantly (Olsen *et al.*, 2003). These observations indicate that landfarming of the sludge will lead to a soil with improved quality.

It is proposed to use the dewatered sludge to cover another problem in Nizhenekamsk, the presence of a site that is used for disposal of solid hazardous waste including spent catalyst, resins, and rubber waste. The site is available for the next 25 years after which it will be returned to the community. It is expected (using the multi compartment model) that in that period of time, the content of oil in the sludge will be further reduced to an amount significantly less than 1000 mg/kg.

A recommendation for physical placement of the sludge on the site in a manner to create a slope of approximately 2% for controlled water drainage into a collection depression and oxygenation of sludge is illustrated in Figure 9.6. The design shown in this figure accomplishes run-on and runoff control and will prevent rainwater and spring snowmelt from contacting and diffusing through the solid hazardous waste toward the ground water. The collected water can be reapplied to the surface when irrigation is needed to provide water for plant growth, or can be pumped to the wastewater treatment plant. This water will be clean if the fast available oil has been degraded.

The amount of precipitation (snow and rain) in Nizhnekamsk is 550 mm. If vegetation is used as part of the cover, this amount of precipitation will be totally evaporated thus minimizing overland flow to the collection depression and optimizing the aerobic status of the sludge cover to allow polishing of the mineral oil and PAHs through biodegradation. The recommendation is made to use intensively rooting vegetation, and suggestions include pine trees (also evaporation in the cold period) or willow trees that are indigenous to the Nizhnekamsk area.

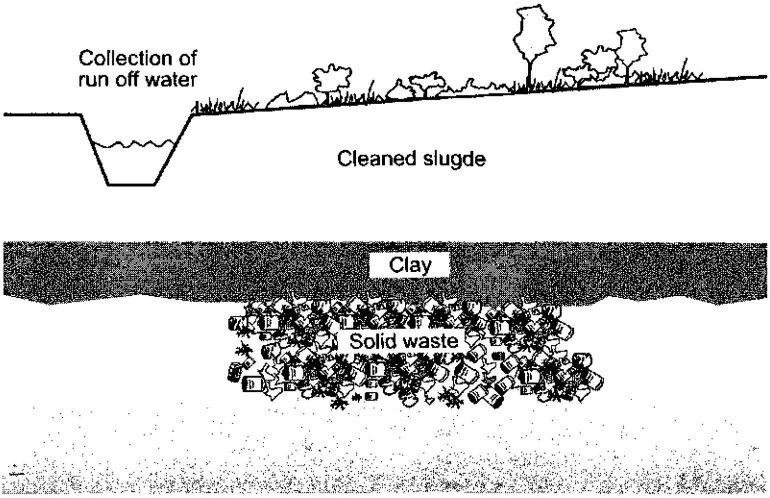

Figure 9.6 Future use of landfarmed sludge on a disposal of solid hazardous waste in Nizhnekamsk.

9.4.6 Four dimensional landfarming

The applications described before are mainly based on application of a relative thin layer, which makes large areas (two dimensions) necessary. As shown, passive landfarming makes use of long periods (third dimension). Adding height will complete this to four dimensions. Using four dimensions may increase the capacity of existing landfarms or reduce the area necessary for cleaning.

Based on the results presented in this thesis and the research of Utah State University on the Libby Ground Water Superfund site in Montana, U.S.A. with three landfarm areas used for soil bioremediation, the concept of four dimensional landfarming has been developed (Harmsen and Sims, 2003). It was concluded that remediation of organic contaminants will continue through depth and time as long as the air filled volume is large enough and contains sufficient oxygen (> 2%) to assure complete aerobic aggregates. The oxygen consumption in a landfarm is the most rapid and largest in the first year and decreases in following years (see Chapter 2). In this first year also easily degradable natural organic matter will be degraded. After one year of treatment it may therefore be possible to add another lift (layer) of contaminated soil to the landfarm and maintain the minimum oxygen condition for continued treatment in the lower layer beneath the most recent lift, even though target remediation values are not achieved in the lower buried lift.

As shown in Chapter 3, it is possible to predict the size of the fast degradable fraction of PAHs using chemical tools. This makes it possible to predict the rate of degradation in a landfarm. Using the three-compartment model and a three-layer application, the development of the PAHs concentration can be predicted when the amounts in the different fractions are known. An example is given in Figure 9.7.

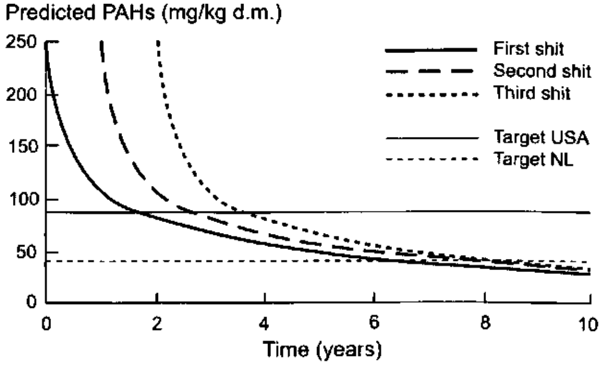

FIGURE 9.7 Prediction using the three compartment model of the PAHs concentration in a four dimensional landfarm. PAHs, 250 mg/kg d.m. Fast available fraction 50%, slow available fraction 35% and very slow available fraction 15%; degradation rate constants respectively: 5; 0.33 and 0.04 y^{-1}. Thickness of each layer 30 cm. Intensive treatment for one season (year).

Figure 9.7 shows that the highest decrease of the PAHs concentration can be expected shortly after application of a lift. Degradation of the slow and very slow degradable fractions requires more time. Especially with low target values (minimal risks), long treatment times are necessary and differences in treatment times of different layers are hardly visible. In this example a target value of 88 mg/kg d.m. (USA-value) has been used. Using one layer this value will be reached after two years. With three layers, all the layers are below this target in 4 years, and the average concentration of all three layers will be even lower. With this target value the capacity of the landfarm has increased to 150%. Having lower target values the profit will be larger. A target value of 40 mg/kg d.m. (Dutch target value) gives a treatment time of 6 years for one layer and 8 years for three layers. This is an increase of the capacity to 225 %. Use of this concept may reduce the area necessary for landfarming and increase the capacity of existing sites. It may also be used to reach lower residual contaminant concentrations in the soil thorough the depth and area (volume) of the landfarm, without reduction of the present capacity of the site.

Application of this concept of 4-dimensional landfarming is only possible when the oxygen concentration in the lower layer is above 2% and aggregates are aerobic. This means that enough air filled pores must be present. The air filled pore volume depends, among other factors on the soil structure and the level of the water table (Chapter 2, Vermeulen *et al.*, 2003). Also the oxygen consumption of the soil itself may limit the number of layers. With low organic sandy sediment or soil and a low water table, it will be possible to use more than 3 layers at 30 cm depth for each layer. With higher clay and organic matter content, and a high water table 4-dimensional landfarming may be restricted to 2 layers.

Summary

Due to the necessity of continuous dredging activities in the Netherlands, there is an enormous supply of contaminated sediments. This situation requires an efficient treatment procedure with low costs and reasonable spatial demands. Landfarming is a treatment technology that offers a good solution. Dredging of waterways is of vital importance for safety, economy and ecology. Without a good water management system to maintain proper depths of waterways, of which dredging is a part, shipping would be difficult. In a low country like the Netherlands great parts would suffer under too wet or too dry conditions if the canal and ditch system, used for discharge of surplus of water and supply of water during dry periods, is not properly maintained. The presence of contaminated sediments can also be a threat for the environment due to the potential release of contaminants from the sediment. Therefore, large quantities of sediments have to be dredged yearly, from large harbour systems to small ditches in the rural area. Since a substantial part of these sediments is too contaminated to be relocated, either in the sea or on land, disposal or treatment is necessary. For the removal of contaminants including PAHs and mineral oil that are present in many sediments, bioremediation is a suitable treatment. PAHs and mineral oil accumulate in sediments because they are not degradable under the existing anaerobic conditions. Although the fraction of sediment that is only contaminated with PAHs and mineral oil is relatively small, the absolute amount is too large for costly treatment procedures. In the Netherlands the policy is to use inexpensive methods like ripening and landfarming, followed by reuse of the treated sediment. Reuse may be as building material, but also as agricultural reuse such as practised in the rural area, where slightly polluted sediments are spread on adjacent land.

Under proper environmental conditions (aerobic), micro-organisms are able to degrade PAHs and mineral oil. In a certain time span, this degradation is limited to the contaminants available for the organisms. If the contaminants are strongly bound to the sediment, a residual concentration remains, which is often substantial and higher than the target value. If the target value is not attained during the set treatment time, reuse is not possible. As shown in long-term experiments carried out on Kreekraksluizen, biodegradation of PAHs and mineral oil is a continuing process and if target values are not attained in the short term (1-2 years), it is possible to obtain them in periods from 5 years to several decades. It will be clear that risks for the environment are reduced during treatment.

Chapter 1 describes the development of landfarming and introduces two main principles and types of landfarming:

- **Intensive landfarming:** processes are optimised using active management activities to reduce contaminants to residual concentrations as quickly as possible.
- **Passive landfarming** with minimal management activities where rapid bioremediation is not necessary, and can be used for reducing residual concentrations.

Which type of landfarming should be used depends on the target value to be reached, the time available, and the area that can be used. Application of both ways of landfarming can transform dredged sediments in reusable soil.

The levels of target values in regulations and possible changes in regulations are important factors for the use of landfarming. Low target values can only be reached in the long-term by using passive landfarming. The higher defined target values can be reached much faster.

It is important to understand and to describe mathematically the limiting processes occurring during landfarming of sediments in order to predict the possibilities for practical application (Chapter 2). PAHs and mineral oil in sediment are strongly ad- or absorbed by the organic matter present in sediment. Limiting conditions for biodegradation that are discussed include; (1) desorption and diffusion of the contaminant within soil aggregates to a place with active micro-organisms, (2) presence of active micro-organisms, and (3) aeration of the dredged sediment.

Desorption and transport in aggregates can be mathematically described using an equation with a sum of first order decreases that include fast, slow and very slow (three-compartment model). The rate constants in this equation not only depend on the organic material into which the contaminants are absorbed, but depend strongly on the moisture content, the radius of the aggregates (respectively quadratic and inverse quadratic relations) and on the pore volume of the sediment. This explains the slow degradation rate in a landfarm, because dry conditions are necessary to have sufficient supply of oxygen, and the possibilities for reducing aggregate sizes on a landfarm are limited.

Within the time frame of landfarming (one year to decades), the presence of micro-organisms is not a limiting factor. Several species of micro-organisms are able to degrade PAHs and mineral oil. Micro-organisms cannot be present in soil pores smaller than their own size; therefore contaminants have to diffuse from these sites to a site with micro-organisms that are able to degrade the contaminant.

The first step in landfarming of dredged sediment is dewatering. During dewatering and ripening of the sediment, water filled pores become air filled pores, which makes supply of oxygen possible. The relevant processes for aeration are modelled. Using the model it is shown that increases of evaporation by cultivation of the sediment or vegetation growing on the sediment are the most important factors. If this extra evaporation is not achieved, landfarming of dredged sediment has to be restricted to thin layers.

Desorption, biodegradation and risks on a landfarm can be predicted using methods developed for measuring the 'bioavailable' fraction. In Chapter 3, the development of bioavailability is described, including a discussion on implementation of the concept. Bioavailability is a concept used to explain the fact that only a certain part of the contaminants are biodegraded in a certain time interval, but is also used to explain effects in bioassays and eco-systems. The ultimate definition of bioavailability does not exist. Bioavailability alone is a confusing term but gets a better meaning if it is used in combination with the word 'for'. Bioavailable for biodegradation is defined as bioavailable for degrading micro-organisms, which are present in small water-filled pores. Several chemical methods are applicable to predict the biodegradable fraction of contaminants and one of them, the Tenax-method, is applied in this thesis.

Landfarming of dredged sediment has been applied from 1990 onwards on the landfarm Kreekraksluizen in the Netherlands. The biodegradation of PAHs on this landfarm is described in Chapter 4. From these long-term experiments it was possible to recognise three degradable fractions; (1) Fast, (2) Slow and (3) Very slow degradable. The degradation rate constants are derived from the measured data. To fully degrade these three fractions requires, respectively, 1 year; about 7 years, and 30-60 years. During fast degradation, the degradation rate depends on the specific PAH. This rate was larger for the low ringed PAHs. During slow and very slow degradation there was no significant difference between the different PAHs. The high molecular weight PAHs (5 and 6 rings) were degraded at the same rate as the low molecular weight (2 and 3 rings) PAHs. The Tenax-method gave a proper prediction of the fast degradable fraction. Kinetic parameters derived from the Tenax-method (a slurry method) showed that processes in an unsaturated landfarm go much slower than in a slurry as follows from the theoretical approach described in chapter 2. Using passive landfarming for a long time, as on the landfarm Kreekraksluizen, low residual concentrations of PAHs have been shown to be possible to achieve.

Chapter 5 describes the biodegradation of mineral oil on the landfarm Kreekraksluizen. It is shown that degradation of mineral oil also follows fast and slow degradation with comparable degradation rate constants as measured for PAHs. It was not possible to recognise a very slow biodegradable fraction. This fraction was not measurable (too small) or the experiments were not continued for a long enough time period. Compared to biodegradation of mineral oil in contaminated soil, mineral oil in contaminated sediment is more difficult to degrade. Biodegradation of mineral oil caused a change in composition; more toxic compounds in the range C_{10}-C_{19} were first degraded and larger, less toxic compounds remained longer in the treated sediment. Using the three-compartment model, predictions of the mineral oil content on the landfarm Kreekraksluizen were made. The residual concentration for the heavily contaminated Petroleum Harbour sediment (original concentration 13,500 mg/kg d.m.) strongly depended on the presence and size of a very slow biodegradable fraction.

Different ways to improve the results of landfarming are described in Chapter 6. During the treatment of sediment on the landfarm Kreekraksluizen, different aspects of landfarming have been optimised. Experiments were focussed on improvement of dewatering, use of higher temperatures, forced aeration, adding of extra organisms in the form of fungi, and use of vegetation. Results of these experiments were compared with the results of the passive landfarm on Kreekraksluizen. It was shown that optimisation only leads to an acceleration of the biodegradation of the fast degradable fraction. This fraction is also degraded on the landfarm in one year, providing no limiting conditions are present. Therefore, optimisation of passive landfarming is not effective in most cases. Optimisation will only be an effective approach if removal of the fast degradable fraction will result in achieving the target value and in case limited space for landfarming is available (which is relevant for short treatment periods).

In forthcoming years, assessment of reuse of treated sediments is expected to be risk-based instead of based on residual concentration. This new assessment procedure should be based on results of generally accepted methods; these are, however, not yet available. Functions of sediment and soil to protect are; (1) the retention function (ability to adsorb contaminants and to prevent mobilisation) and (2) the habitat function (optimal function of soil living organisms). Risks on Kreekraksluizen have been studied by measuring leaching, application of several bio-assays, and monitoring biological activity in general (Chapter 7). Risks for the retention function were followed by using bio-assays with water dwelling organisms and by measuring leaching. These risks decreased very rapidly during dewatering. Based on the experiments, a simple approach for protection of the underlying soil has been developed. The risk for the habitat function decreased more slowly. Small effects in bio-assays were still measurable after 7 years of treatment. No measurable risks were present in the longest (12 years) treated sediments. One of these sediments still contained a large concentration of PAHs then, but the available fraction (measured using the Tenax-method) was low). About 5 years were necessary to achieve a shift from sediment adapted populations of organisms to populations that are to be expected in clean soil.

Because PAHs and mineral oil contaminated sediment can be remediated, negative effects are only present for a limited period. Mixing sediment in a low amount with agricultural or natural soil may therefore be acceptable (Chapter 8). In fact this has already been practised for a long period in the Netherlands. Slightly polluted sediments from ditches in the rural area were and are still spread over adjacent land. In experiments on the island of Goeree-Overflakkee, it has been shown that the practise of spreading of thin layers also led to fast, slow and very slow degradation of the PAHs present. The historical practise of spreading had led to a small increase of the PAHs-concentration alongside the ditch. Using the three-compartment model and measured (Tenax-method) bioavailabilities, it is shown that the accumulation of PAHs in the agricultural soil due to addition of sediment stabilised after 5 dredgings and spreadings of sediment on agricultural land (30 years), which is also the real situation on Goeree-Overflakkee. Short time risks, especially for grazing cattle, can be present during the first spring after spreading of the sediment.

In the final Chapter 9, results of the previous chapters on biodegradation of PAHs and mineral oil contaminated sediment are reviewed. This review is combined with a discussion of the effects of the presence of heavy metals. These heavy metals are not the subject of this thesis but are present in many sediments. Possibilities of reducing risks of heavy metals in combination with landfarming are given.

Chapter 9 concludes with a description of possible applications of passive landfarming. Because passive landfarming requires a long time period, this approach should be combined with beneficial use of the area. Examples described are the combination with nature development, use in constructions, combination with growing of biomass for energy production, and use as cover of a landfill. The necessity of biodegradation of PAHs present in the flood plains of large Dutch rivers is also discussed. This chapter ends with the description of four-dimensional landfarming, in which the number of applied layers of sediment on a landfarm is increased in order to minimise the area needed for passive landfarming.

Samenvatting

Zonder een goed onderhoud zullen diverse watersystemen in Nederland langzaam dichtslibben en kunnen dan hun functie niet meer vervullen. Dit kan leiden tot economische schade, wateroverlast en achteruitgang in kwaliteit en biodiversiteit van ecosystemen. Onderhoud door middel van baggeren (uitdiepen en verwijderen van de waterbodem) is daarom noodzakelijk. In het verleden werd de geproduceerde onderhoudsbaggerspecie naar zee gebracht, gebruikt voor het ophogen en egaliseren van land en verspreid op landbouwpercelen. Baggerspecie is momenteel echter vaak verontreinigd en het is nodig deze onderhoudsbaggerspecie op een andere wijze te verwerken, bij voorkeur met technieken die weinig kosten en een klein beslag leggen op beschikbare ruimte. Hiernaast kan het noodzakelijk zijn verontreinigde baggerspecie te verwijderen en te reinigen, omdat de specie direct gevaar oplevert voor mens, dier en ecosystemen. Tot 2010 zal in Nederland 250 miljoen kubieke meter licht tot zwaar verontreinigde baggerspecie moeten worden verwerkt. Deze specie is afkomstig uit de vele rivieren, kanalen, havens, meren en sloten. De meest voorkomende verontreinigingen zijn zware metalen als cadmium, zink en lood, polycyclische aromatische koolwaterstoffen (PAK's) en minerale olie. PAK's ontstaan bij onvolledige verbranding, minerale olie is een verzamelterm voor olieproducten afkomstig van aardolie. PAK's en minerale olie zijn biologisch afbreekbaar en kunnen door micro-organismen in de bodem worden omgezet in onschuldige verbindingen. Bij de afbraak gebruiken de micro-organismen zuurstof. Zuurstof ontbreekt in waterbodems, waardoor accumulatie (opeenhoping) plaats vindt van PAK's en minerale olie.

Biologische reiniging van met PAK's en minerale olie verontreinigde baggerspecies levert een schoon product, dat kan worden hergebruikt. Hoewel veel baggerspecie ook niet afbreekbare zware metalen bevat is er voldoende baggerspecie verontreinigd met alleen PAK's en minerale olie om toepassing van biologische technieken te rechtvaardigen. In het Nederlandse beleid wordt er de voorkeur aan gegeven om verontreinigde baggerspecie te verwerken via goedkope technieken en vervolgens te hergebruiken als bouwstof of schone grond.

Landfarmen is een effectieve biologische manier om baggerspecie, verontreinigd met PAK's en minerale olie, te reinigen. Het is een biologische reinigingstechniek, waarbij verontreinigde grond of baggerspecie in een laagdikte van 30-100 cm op de bodem wordt verspreid. De aanvoer van de voor afbraak noodzakelijke zuurstof worden gestimuleerd door middel van bewerken van de bodem of aanwezigheid van begroeiing. Gedurende de behandelingsperiode beperkt de afbraak zich tot die verontreinigingen die beschikbaar zijn voor de micro-organismen. De verontreinigingen, die sterk gebonden zijn aan de baggerspecie, breken langzamer af. De hoeveelheid (restconcentratie), die achterblijft na een behandelingsperiode van een jaar, kan te hoog zijn om te voldoen aan de criteria die zijn gesteld voor hergebruik. In dit onderzoek zijn een aantal landfarmingsexperimenten op Kreekraksluizen langdurig (tot 12 jaar) gevolgd. Dit onderzoek heeft aangetoond dat de afbraak van PAK's en minerale olie in baggerspecie behandeld op een landfarm doorgaat en dat op langere termijn lage restconcentraties kunnen worden verkregen.

Hoofdstuk 1 van dit proefschrift beschrijft de ontwikkeling van de twee belangrijke vormen van landfarmen:

- **Intensief landfarmen**: Door middel van actief management van de landfarm worden processen in de landfarm geoptimaliseerd om het gehalte aan verontreinigingen zo snel mogelijk te reduceren.
- **Extensief landfarmen**: Activiteiten op de landfarm worden zoveel mogelijk geminimaliseerd. Het wordt toegepast als snelheid van het proces niet van belang is of om de restconcentratie, nog aanwezig na intensief landfarmen, verder omlaag te brengen. In de Engelse taal wordt voor extensief landfarmen de term 'passive landfarming' gebruikt.

Welke vorm van landfarmen moet worden gebruikt hangt af van de eindconcentratie van de verontreiniging die moet worden bereikt, de beschikbare tijd en de ruimte die beschikbaar is. Beide vormen van landfarmen veranderen baggerspecie in herbruikbare grond.

Het niveau van de te bereiken concentraties, vastgelegd in regelgeving en mogelijke veranderingen in regelgeving, zijn belangrijke factoren bij toepassing van landfarmen. Lage concentraties (multifunctioneel hergebruik) kunnen alleen op lange termijn worden bereikt door toepassing van extensief landfarmen. Hogere concentraties, waarbij wordt voldaan aan de criteria voor hergebruik als bouwstof, kunnen veel sneller worden bereikt.

Het is belangrijk beperkende factoren in een landfarm te begrijpen en wiskundig te beschrijven, om te kunnen sturen en te voorspellen wat de effecten van praktische toepassing van landfarmen zijn (Hoofdstuk 2). PAK's en minerale olie in baggerspecie zijn sterk geadsorbeerd aan of geabsorbeerd in de organische stof, die aanwezig is in de baggerspecie. Factoren, die bepalend zijn voor de biologische afbraaksnelheid, zijn; (1) desorptie en diffusie van verontreinigingen in bodemaggregaten naar een plek met actieve micro-organismen, (2) aanwezigheid van actieve micro-organismen en (3) de introductie van zuurstof in de baggerspecie.

Het is mogelijk desorptie en diffusie in bodemaggregaten te beschrijven met een wiskundige vergelijking bestaande uit een combinatie van drie eerste orde afnamen van snel, langzaam en zeer langzaam desorbeerbare fracties (driecompartimentenmodel). De snelheidscoëfficiënten in deze vergelijking hangen niet alleen af van de organische stof waarin de verontreinigingen zijn geabsorbeerd, maar worden ook in sterke mate bepaald door het vochtgehalte, de straal van de aggregaten (respectievelijk een kwadratische en een omgekeerd kwadratische relatie) en het porievolume. Deze relaties verklaren de langzame afbraak in een landfarm. In een landfarm moet het vochtgehalte laag zijn om voldoende aanvoer van zuurstof mogelijk te maken. Verder is het onmogelijk de grootte van de aggregaten aanzienlijk te reduceren met behulp van standaard landbouwkundige bewerkingen.

In de tijd, die benodigd is voor landfarmen (één tot tientallen jaren), is de aanwezigheid van afbrekende micro-organismen geen beperkende factor. Verschillende micro-organismen, die al aanwezig zijn in de baggerspecie en micro-organismen, die zich verder ontwikkelen in de grond ontstaan gedurende landfarmen, zijn in staat PAK's en minerale olie af te breken. Micro-organismen kunnen echter niet aanwezig zijn in poriën in sediment en bodem die kleiner zijn dan zijzelf, waardoor verontreinigingen aanwezig in kleine poriën zich moeten verplaatsen naar poriën met actieve micro-organismen.

De eerste stap bij landfarmen van baggerspecie is ontwateren van de specie, waardoor watergevulde poriën worden vervangen door luchtgevulde poriën. Hierdoor wordt een snellere aanvoer van de voor afbraak benodigde zuurstof mogelijk. In een wiskundig model zijn de relevante processen voor de aëratie beschreven. Dit model laat zien dat stimulering van de verdamping de belangrijkste factor is. Dit kan worden gerealiseerd door het regelmatig omzetten van de baggerspecie of door stimulering van de groei van vegetatie. Als deze extra verdamping niet kan worden gerealiseerd, moet landfarmen van baggerspecie worden beperkt tot uitvoering in dunne lagen.

Desorptie, biologische afbraak en risico's op een landfarm kunnen worden voorspeld door gebruik te maken van methoden voor het meten van de 'biologisch beschikbare fractie' van de aanwezige verontreinigingen. In Hoofdstuk 3 wordt de ontwikkeling van het concept biobeschikbaarheid beschreven, samen met een discussie over het gebruik en de invoering van biobeschikbaarheid in regelgeving. Biobeschikbaarheid wordt gebruikt om te verklaren dat in een bepaalde tijdsperiode niet alle verontreiniging is afgebroken, maar dat een deel onaangetast blijft. Het wordt ook gebruikt voor het verklaren van effecten in bio-assays en ecosystemen. Een alles omvattende definitie van biobeschikbaarheid bestaat niet. Biobeschikbaarheid alleen is een verwarrende term. Het krijgt betekenis als het wordt gebruikt in combinatie met het woord 'voor'. Biobeschikbaarheid voor biologische afbraak wordt dan gedefinieerd door beschikbaarheid voor afbrekende micro-organismen, die aanwezig zijn in kleine watergevulde poriën. Er bestaan diverse chemische methoden om de fractie beschikbaar voor biologische afbraak te voorspellen. Eén van deze methoden, de Tenaxmethode, is toegepast in het onderzoek beschreven in dit proefschrift.

Landfarmen van verontreinigde baggerspecie wordt al vanaf 1990 toegepast op de experimentele landfarm Kreekraksluizen, gelegen bij de gelijknamige sluizen in het Schelde-Rijnkanaal in de provincie Zeeland. De biologische afbraak van PAK's, gemeten in verschillende baggerspecies op deze landfarm, is beschreven in Hoofdstuk 4. Door de lange duur van de experimenten was het mogelijk drie afbreekbare fracties te onderscheiden, die met verschillende snelheden afbreken; (1) snel, (2) langzaam en (3) zeer langzaam. De bijbehorende afbraakconstanten (eerste orde afbraak) zijn afgeleid uit de gemeten PAK-gehalten. Voor de volledige afbraak van de verschillende fracties zijn perioden nodig van respectievelijk 1, circa 7 en 30 tot 60 jaar. Gedurende de eerste periode van snelle afbraak was de waargenomen afbraaksnelheid afhankelijk van het type PAK. De kleinere PAK's (bestaande uit twee en drie aromatische ringen) braken het snelst af. Afbraak van PAK's met 4 en vooral met 5 en 6 ringen gaat langzamer. Gedurende de opvolgende langzame en zeer langzame afbraak kon dit onderscheid niet meer worden gemaakt en braken alle PAK's even langzaam af.

De resultaten van desorptiemetingen met de Tenaxmethode gaven een goede voorspelling van de snel afbreekbare fractie. Kinetische parameters, afgeleid van de meetresultaten van de Tenaxmethode, lieten zien dat de desorptieprocessen in een met water verzadigd systeem (zoals bij de Tenaxmethode) beduidend sneller gaan dan de afbraakprocessen in een met water onverzadigde landfarm. Dit kon worden verklaard met behulp van de theorieën beschreven in hoofdstuk 2.

Hoofdstuk 5 beschrijft de biologische afbraak van minerale olie op de landfarm Kreekraksluizen. De afbraak van minerale olie verliep via snelle en langzame afbraak. Vergelijkbare afbraakconstanten met die gevonden voor de PAK's konden worden afgeleid voor de onderzochte baggerspecies. Het was niet mogelijk een zeer langzaam afbreekbare fractie te herkennen. Vergeleken met de biologische afbraak van minerale olie in verontreinigde bodem, verloopt de afbraak van minerale olie in baggerspecie langzaam. Dit wordt veroorzaakt door de wijze waarop minerale olie terechtkomt in de waterbodem. Olie is eerst aanwezig als drijflaag en wordt via het bovenstaande water getransporteerd naar de waterbodem. Op weg hier naar toe vervluchtigen gemakkelijk afbreekbare componenten en worden gemakkelijk afbreekbare componenten afgebroken. Er blijft een verweerde olie over, die moeilijker afbreekbaar is. Dit in tegenstelling tot een met olie verontreinigde bodem, waarin de oorspronkelijke minerale olie meestal nog herkenbaar is. Door biologische afbraak in baggerspecie op een landfarm verandert de samenstelling van minerale olie verder. De meeste toxische verbindingen (koolwaterstoffen met tussen de 10 en 19 koolstofatomen) worden het eerst afgebroken en minder toxische verbindingen met meer koolstofatomen blijven langer aanwezig.

Met het driecompartimentenmodel zijn voorspellingen gemaakt van het minerale oliegehalte op de landfarm Kreekraksluizen. Het resterende minerale oliegehalte na landfarmen van de zwaar verontreinigde baggerspecie uit de Petroleumhaven (oorspronkelijk minerale oliegehalte 13.500 mg/kg droge stof) hangt sterk af van de aanwezigheid en grootte van een zeer langzaam afbreekbare fractie.

Verschillende manieren om de resultaten van landfarmen te verbeteren zijn beschreven in Hoofdstuk 6. Verbetering is te beschrijven als een lagere restconcentratie van de verontreiniging, bij voorkeur in minder tijd en tegen redelijke kosten. De experimenten waren gericht op optimalisatie van procesfactoren zoals ontwatering, verhoogde temperatuur, geforceerde beluchting, toevoeging van extra organismen in de vorm van schimmels en gebruik van vegetatie. Resultaten van deze experimenten zijn vergeleken met het doorlopende extensieve landfarm experiment op Kreekraksluizen. Optimalisatie is alleen effectief voor versnelling van de afbraak van de snel afbreekbare fractie. Omdat deze fractie wordt ook afgebroken op de extensieve landfarm binnen één jaar, is optimalisatie van extensief landfarmen meestal niet effectief. Optimalisatie is effectief als door het verwijderen van deze snel afbreekbare fractie wordt voldaan aan de criteria voor hergebruik en er weinig ruimte voor landfarmen beschikbaar is. Verkorten van de behandelingsperiode vergroot dan de verwerkingscapaciteit van de betreffende locatie.

In de komende jaren zal er waarschijnlijk een verschuiving optreden in de beoordeling van hergebruik van gereinigde baggerspecie: van een beoordeling op basis van nog aanwezige concentraties van de verontreinigingen naar een op risico's gebaseerde beoordeling. Een dergelijke nieuwe beoordeling moet gebaseerd zijn op algemeen geaccepteerde methoden. Deze zijn echter nog niet beschikbaar. Functies van de (water)bodems die beschermd moeten worden zijn; (1) de retentiefunctie; de eigenschap om verontreinigingen te adsorberen en mobilisatie van de verontreinigingen naar grond- en oppervlaktewater te voorkomen en (2) de habitatfunctie; het optimaal functioneren mogelijk maken van de in de bodem functionerende flora en fauna. Risico's op de landfarm Kreekraksluizen zijn bestudeerd door het meten van uitspoeling, het meten van mogelijke ecotoxiciteit met diverse bio-assays en het meten van diverse biologische activiteiten (Hoofdstuk 7). Risico's voor de retentiefunctie zijn gevolgd door het meten van uitspoeling en de toepassing van bio-assays, die gebruik maken van in de waterfase levende organismen. Deze risico's bleken snel te verminderen gedurende het ontwateren van de baggerspecie. Gebaseerd op deze experimenten is een eenvoudig beheersconcept ontwikkeld voor de bescherming van de onderliggende grond op een landfarm. De risico's voor de habitatfunctie nemen langzamer af. Kleine effecten in de onderzochte species waren nog meetbaar na 7 jaar landfarmen, als gebruik werd gemaakt van bio-assays met in de bodem levende organismen. Geen meetbare effecten zijn waargenomen in de baggerspecies die al twaalf jaar zijn behandeld. Eén van deze baggerspecies bevatte nog steeds een relatief hoge concentratie PAK's, maar de beschikbare fractie hiervan (gemeten met de Tenaxmethode) was klein. Er was circa 5 jaar nodig voordat een gemeenschap van organismen aanwezig in de onderzochte baggerspecies, is gewijzigd in een gemeenschap van organismen die verwacht mag worden in een gezonde grond.

Omdat PAK's en minerale olie via biologische afbraak verdwijnen uit baggerspecie, zullen gedurende een beperkte periode toxische effecten merkbaar zijn. Mengen van beperkte hoeveelheden baggerspecie met landbouwgrond of grond in natuurgebieden kan dan een acceptabele oplossing zijn (Hoofdstuk 8). In feite is het verspreiden van baggerspecie op landbouwgrond een praktijk die al eeuwenlang wordt toegepast in Nederland. Ook nu nog worden schone baggerspecie, maar ook licht verontreinigde baggerspecie, uit gebaggerde watergangen in het landelijke gebied verspreid over aanliggende percelen. Baggeren om de watergangen op diepte te houden vindt om de 6 tot tien jaar plaats. Met een experiment uitgevoerd op Goeree-Overflakkee is aangetoond dat bij het verspreiden van met PAK's verontreinigde baggerspecie, de afbraak van PAK's ook beschreven kan worden in termen van snelle, langzame en zeer langzame afbraak. Het verspreiden van baggerspecie in het verleden heeft geleid tot een lichte verhoging (accumulatie) van het PAK-gehalte in een strook langs de gebaggerde watergang. Door gebruik te maken van het driecompartimentenmodel en biobeschikbaarheden, gemeten met de Tenaxmethode, is aangetoond dat de accumulatie van PAK's in de met bagger belaste strook stabiliseert na 5 keer verspreiden van de bagger. Dit komt overeen met een periode van 30 jaar en een aantal van de bemonsterde locaties voldeed hieraan. Korte termijn risico's, speciaal voor grazend vee, kunnen aanwezig zijn gedurende de eerste lente na het verspreiden van de bagger.

In het laatste Hoofdstuk 9 zijn alle resultaten over de biologische afbraak van PAK's en minerale olie uit de voorgaande hoofdstukken geëvalueerd en bediscussieerd. Dit is gecombineerd met een discussie over de effecten en aanwezigheid van zware metalen. Hoewel zware metalen niet het onderwerp zijn van dit proefschrift, mocht deze discussie niet ontbreken, omdat vele met PAK's en minerale olie verontreinigde baggerspecies ook verontreinigd zijn met zware metalen. Mogelijkheden zijn beschreven om de risico's van zware metalen in combinatie met landfarmen te verlagen.

Hoofdstuk 9 eindigt met een perspectief voor de toepassing van extensief landfarmen. Omdat met extensief landfarmen veel tijd is gemoeid, moet het worden gecombineerd met een nuttige toepassing van de in gebruik genomen ruimte. Dit is niet alleen om de kosten te verlagen, maar ook om niet onnodig beslag te leggen op schaarse ruimte. Beschreven voorbeelden zijn de combinatie met natuurontwikkeling, gebruik in constructie als geluidswallen, wegen en dijken, combinatie met de teelt van biomassa voor de productie van bio-energie en het toepassen van extensief landfarmen op een vuilstort om een schone afdeklaag te maken, die bovendien als extra bescherming dient. Ook is ingegaan op de mogelijkheid van biologische afbraak van PAK's in de bodem van de uiterwaarden van de grote Nederlandse rivieren. Dit hoofdstuk eindigt met de beschrijving van vierdimensionaal landfarmen, waarbij het aantal te landfarmen lagen wordt geoptimaliseerd om de benodigde ruimte en tijd voor extensief landfarmen te minimaliseren.

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