Organic Contaminants in Soil

Desorption Kinetics

and Microbial Degradation

promotor: dr. W. H. van Riemsdijk,
hoogleraar in de bodemscheikunde en chemische grond- en gewasanalyse

co-promotor: dr. ir. G. Schraa,
universitait docent bij het Laboratorium voor Microbiologie

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Desorption Kinetics

and Microbial Degradation

Wendela Schlebaum

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Stellingen

I

De analogie tussen humuszuren en surfactant-micellen gaat niet meer op bij het beschrijven van de kinetiek van de interacties tussen organische verontreinigingen en humuszuren.

Wershaw, R.L. Model for humus in soil and sediments. Environ. Sci. Technol. 1993, 27: 814-816.

II

De fysische betekenis van modellen die vertraagde poriediffusie van organische verontreinigingen in bodemdeeltjes beschrijven, wordt overschat.

III

Humine speelt een belangrijke rol bij de trage desorptie van organische verontreinigingen uit bodems.

dit proefschrift

IV

De door Carroll et al. berekende diffusie-afstanden zijn van weinig waarde aangezien een goede fit van een enkele continue desorptiecurve van een organische verontreiniging uit een bodem geen betekenisvolle parameters oplevert.

Carroll, K.M.; Harkness, M.R.; Bracco, A.A.; Balcercel, R.R. Application of a permeant/polymer diffusional model to the desorption of polychlorinated biphenyls from Hudson River sediments. Environ. Sci. Technol. 1994, 28: 253-258.

V

Onderzoeksresultaten waarbij een lagere dosis van een stof een meer ongewenst effect geeft dan een hogere dosis werpen een ander licht op de uitspraak "er zijn geen giftige stoffen, er zijn alleen giftige doses".

Environmental News. Results of low-dosure exposure research may challenge the theoretical basis of toxicology. Environ. Sci. Technol. 1998, 485A-486A.
Ashford, N.A.; Miller, C.S. Low-level chemical exposures: a challenge for science and policy. Environ. Sci. Technol. 1998, 508A-509A.

VI

Biologische beschikbaarheid is een tijdsafhankelijke parameter.

VII

Zinloos geweld is een pleonasme.

VIII

De eigen keuze van een woonplaats hoeft niet beloond te worden met een reiskostenvergoeding.

IX

Het gezegde *a gentleman never sails to windward* is geen vrijbrief voor het gebruik van de motor van een zeiljacht.

X

De damesrugbycompetitie zou gebaat zijn bij de diskwalificatie van teams die bij een wedstrijd niet genoeg speelsters kunnen opstellen.

XI

Per saldo worden de wachtgeldkosten van de universiteit niet verminderd door het inhuren van een "outplacementbureau" voor AIO's/OIO's.

XII

Dragers van een korte broek zullen minder snel staand plassen.

Stellingen behorende bij het proefschrift "Organic Contaminants in Soil: Desorption Kinetics and Mirobial Degradation".
Wendela Schlebaum, Wageningen, 19 februari 1999.

Contents

CHAPTER 1

Introduction

Contaminating soils is far less complicated than cleaning contaminated soils. It is also far less expensive. The Dutch government has estimated that the cost of cleaning or remediating the known contaminated sites in the Netherlands, would be a hundred billion guilders [52]. For sites polluted with organic contaminants, soil micro-organisms could provide a less costly biological remediation method especially when the remediation can occur on the site without excavation of the soil, so-called in situ bioremediation. Under the proper environmental conditions, most organic contaminants can be degraded by micro-organisms. Environmental conditions as pH, temperature, salt concentration, water availability, essential nutrients, availability of oxygen, and redoxpotential, influence the microbial activity. The environmental conditions can sometimes be altered in the soil to create an optimal environment for a certain micro-organism or a range of micro-organisms. However, even under optimal conditions bioremediation can be hampered as the pollutants do not seem to be available to the micro-organisms [3]. The organic contaminants appear to be sequestered within the soil matrix. Sorption and desorption kinetics of the organic contaminants in soil can therefore control the possible success of bioremediation.

Sorption and desorption kinetics are complex and poorly predictable at present [62]. In this introductory chapter, current opinions on mechanisms behind sorption and desorption kinetics and the importance of desorption kinetics for microbial degradation of organic contaminants in soil are discussed. A factor that has been shown to control the sorption of organic contaminants in soil is the organic matter or organic carbon content of a soil. The minerals present in the soil only start to play a role below an organic carbon content of 0.1% [72]. However, even at virtually unmeasurable levels, the extent of sorption can be dominated by organic matter [72]. Several aspects of soil organic matter that are relevant for sorption of organic contaminants are introduced in this chapter.

The aim of this research was to investigate sorption and desorption kinetics of organic contaminants in soil and specifically the possible role of natural organic matter and the influence of sorption and desorption kinetics on the microbial degradation rates of these contaminants. Although this research focuses on processes occurring in soil, processes occurring in

sediments will have similar features. In this study, a chlorinated benzene (pentachlorobenze) and a polychlorinated biphenyl (2,5-dichlorobiphenyl) were used as model compounds. Industrially produced chlorinated benzenes and polychlorinated biphenyls (PCBs) have been detected in many environmental samples as soils, groundwater, sediments and animals, see e.g. [45, 57, 72].

SOIL ORGANIC MATTER

Soil organic matter is the result of the biological and chemical decomposition of dead plant and animal remains in soil. After successive alterations and cross-linkages, products are formed that no longer bear resemblance to the plants and animals. These products are referred to as natural organic matter or humus. Stevenson [74] gave the following definition of natural organic matter in soil: the total of organic compounds, exclusive of undecayed plant and animal tissues, their "partial decomposition" products and the soil biomass [74]. Organic contaminants in soil increase the organic matter or organic carbon content of a soil, especially in case of an oil spill. In most cases, however, the contribution of organic contaminants to the natural organic matter content is negligible.

The formation process of natural organic matter already indicates that the structure and content of organic matter depends on time, climate, vegetation, parent material, topography. Natural organic matter is therefore a heterogeneous and complex substance for which no exact chemical or physical structure can be given. Natural organic matter can be present in soluble form in the soil solution, or as insoluble organic matter. Soluble organic matter is often referred to as Dissolved Organic Carbon (DOC). The DOC content in the soil solution is usually rather low compared to the solid organic carbon content. Insoluble organic matter can be retained in the soil (1) as insoluble macromolecular complexes, (2) as macromolecular complexes bound together by divalent and trivalent cations, such as Ca^{2+}, Fe^{3+}, and Al^{3+}, (3) bound to clay minerals, e.g. through bridging by polyvalent cations (clay-metal-humus) or hydrogen bonding, and (4) as organic substances held within the interlayers of expanding-type clay minerals [74]. In agricultural soils of the temperate zone, most of the organic matter is intimately bound to clay minerals [74].

Natural organic matter has been operationally divided into fulvic acids, humic acids and humin. Fulvic acids are soluble in both acidic and alkali solutions, humic acids are only soluble in alkali solutions and humin is not soluble at all. Fulvic acids and humic acids, often referred to as humic substances, have been extensively studied while the insolubility of humin

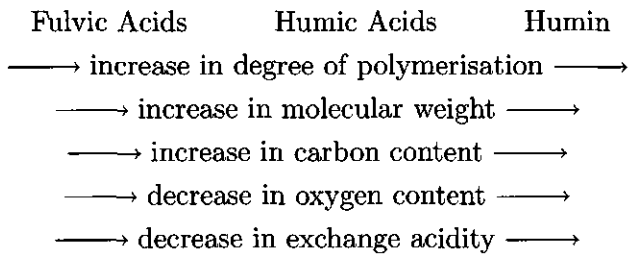

FIGURE 1.1. Chemical properties of the different soil organic matter fractions. Adapted from Stevenson [74].

has limited its chemical characterisation [33]. All fractions are part of a heterogeneous mixture of molecules that show a wide range in any given property, e.g. the molecular weight can range from as low as several hundred to perhaps over 300,000 [74]. Some properties of the different organic matter fractions are shown in Figure 1.1.

Fulvic Acids and Humic Acids

Humic substances have a high content of oxygen-containing functional groups, including COOH, phenolic OH, alcoholic OH, and C=O in quinones, hydroxyquinones, and ketones. The total acidity of humic acids (5.6–8.9 eq kg^{-1}) is lower than that of fulvic acids (6.4–14 eq kg^{-1}) [74]. The lower reactivity of humic acids results from a decrease in oxygen content and an increase in carbon content. With an increase in carbon content of the macromolecules their hydrophobicity will also increase. The average range in molecular weights of humic acids is in the order of 20,000 to 100,000, with few molecules having a molecular weight greater than 250,000 or smaller than 10,000 [74]. The range in molecular weight is less wide for fulvic acids. A "typical" fulvic acid will have a molecular weight in the order of 500 to 2000 [74].

Humic acids can be envisioned as rather long-chain macromolecules, with two-dimensional or three-dimensional cross-linkages, that can adopt the configuration of a flexible coil in solution. The shape of the molecule in solution is strongly influenced by factors as pH and salt concentration. Under neutral or slightly alkaline conditions, the molecules are in expanded state due to mutual repulsion of charged acidic groups; at low pH, and in the presence of a high electrolyte concentration, contraction occurs through reduction in repulsive forces. Fulvic acids can be considerably smaller than humic acids, swelling and shrinking of the three-dimensional structure is

therefore limited. Humic substances have also been visualised as micelles or ordered aggregates of molecules [83]. Each humic acid is then proposed to consist of a number of molecules that have both a hydrophobic and a hydrophilic part. In aqueous solutions, the exterior surface of the humic acid is formed by the hydrophilic parts of the molecules and the hydrophobic parts form the interior surface. The hydrophobic interiors of the micelles or membranes can serve as a hydrophobic phase into which non-ionic organic chemicals can "dissolve" [83].

Fulvic acids and humic acids are normally present as insoluble organic matter, but they can also be part of the DOC in the soil solution. Fulvic acids and humic acids can form 10% to 70% of the DOC in the soil solution.

Humin

Humin is traditionally obtained as the residue which remains after a sample is stirred with an alkaline aqueous solution and then centrifuged [66]. This fraction will therefore also contain a significant amount of mineral matter. HF/HCl extraction can reduce the mineral content but part of the mineral fraction is intimately associated with humin. Rice and MacCarthy [64–66] have developed a method to separate humin into the following three compound classes; (1) a fraction that can be extracted with an organic solvent in a Soxhlet apparatus and which is referred to as "bitumen" (bitumen is a tar-like mixture of hydrocarbons derived from petroleum), (2) a bound lipid fraction, and (3) a bound humic acid fraction. The bound humic acid conforms to the operational definition of humic acid but it is only released after disaggregation of humin [66]. Rice and MacCarthy [66] propose that humin can be viewed as an aggregation of bitumen, bound humic acid, bound lipids and an inorganic fraction. None of these fractions, by itself, conforms to the operational definition of humin; an acid- and alkali-insoluble organic material [66].

13C-NMR studies have revealed that paraffinic (alkanes) and aromatic structures are major components of humin [33]. Not much is known of the molecular weight, size and shape of humin. It is however expected that humin molecules are considerably larger and more hydrophobic than fulvic and humic acids.

Sorption of Organic Contaminants to Organic Matter

Sorption of non-ionic organic chemicals such as chlorinated benzenes and polychlorinated biphenyls to soil organic matter, is expected to occur mainly via rather non-specific mechanisms as hydrophobic interactions, hydrogen bonding and van der Waals interactions. The sorption of organic

contaminants to organic matter is therefore often considered as a partitioning process in which the contaminant dissolves in the hydrophobic phase that is formed by organic matter. The hydrophobicity and size of the organic matter is therefore expected to play a role in the affinity and sorption capacity of organic matter for organic contaminants.

The characteristics of fulvic acids, humic acids and humin suggest that the affinity for non-ionic organic contaminants will increase going from fulvic acids, via humic acids to humin. Whether the increase in affinity also corresponds with a measurable decrease in release rates of organic contaminants from these fractions is unknown. The influence of the sorption of organic contaminants to organic matter on the release rates of these contaminants from soils is discussed in the following section. In Chapter 2 and Chapter 4 of this thesis, the affinity and the release rates of an organic contaminant from humic acids, bound humic acids and humin are investigated.

DESORPTION KINETICS OF ORGANIC CONTAMINANTS IN SOIL

Several reviews on sorption and desorption kinetics of organic contaminants in soil can be found in literature [9, 10, 46, 62, 80]. Desorption kinetics generally show an initial fast period and a subsequent period of slow desorption, where slow can imply time scales of decades, see e.g. [76]. The slow desorbing fraction of organic contaminants increases with increasing residence time ("ageing") of the contaminant in the soil. This is indicative of a slow uptake process. Since specific sorbate-sorbent interactions do not seem possible for the sorption of non-ionic organic contaminants to soils, chemical interactions are not believed to play a role in the slow release of these contaminants from soil. Therefore, processes involving diffusive mass transfer have been proposed to cause slow release rates [9, 46, 62].

Proposed mechanisms include intraorganic matter diffusion and retarded diffusion through intraparticle nanopores. Intraorganic matter diffusion models assume that diffusion through natural organic matter matrices is the rate determining step in the desorption of organic contaminants from soils [62]. Two categories of expanded and condensed organic matter have been distinguished to explain the observed fast and slow desorption kinetics of organic contaminants from soils [14, 46, 62]. Retarded intraparticle pore diffusion models assume that the rate-limiting process is molecular diffusion in porewater within mineral components that is retarded by local adsorption on pore walls [62]. Adsorption on the pore walls may occur as partitioning into soil organic matter or as adsorption to a mineral surface.

It is very likely that intraorganic matter diffusion and retarded intraparticle pore diffusion operate simultaneously [46, 62].

The importance of natural organic matter for slow desorption kinetics of organic contaminants in soil has been questioned since studies with a commercial humic acid showed that desorption was very fast and without a slow desorbing organic contaminant fraction [32, 48]. In Chapter 2 of this thesis, desorption kinetics of a natural humic acid and an organic contaminant (pentachlorobenzene) are examined. To test whether intraorganic matter diffusion can be the rate-determining step in the desorption behaviour of a soil, the desorption behaviour of different organic matter fractions are compared to that of a soil (Chapter 4). In Chapter 3 of this thesis, the desorption kinetics of a soil are investigated.

DESORPTION KINETICS AND MICROBIAL DEGRADATION IN SOIL

The limited availability of organic contaminants for micro-organisms has been proposed to hamper bioremediation of contaminated soils. Alexander [3] has collected information available in literature on the biological availability of organic contaminants and shows that:

1. the availability of organic chemicals in soil to micro-organisms in the field declines markedly with time,
2. freshly added chemicals are readily available to micro-organisms in soil while the same chemicals that have a long residence time in the soil are not metabolised,
3. with increasing residence time organic compounds added to sterile soil become increasingly less available to subsequently added micro-organisms,
4. some compounds become increasingly resistant with time to extraction, and
5. sorption and desorption of hydrophobic compounds often require long periods to reach equilibrium.

Ogram et al. [55] demonstrated that sorbed chemicals were completely protected from microbial degradation while dissolved chemicals were degraded. This implies that sorption can have a large influence on the degradation of organic contaminants in soil. Sorption of organic contaminants to the soil can limit degradation in two ways. First, sorption decreases the concentration of the contaminant in the aqueous phase and second, the contaminants may be released so slowly from the soil that the release rates limit biodegradation.

The influence of the release rates of organic contaminants from soil depends on the ratio between the release rates and the intrinsic activity of the micro-organisms. The intrinsic activity of the micro-organisms, as determined by the rate of uptake and metabolism of the cells [7], will depend on environmental conditions. When the intrinsic activity is slower than the release rate, the activity of the micro-organisms will limit the degradation of contaminants in soil. Note that in that case, the availability of the contaminant for the micro-organisms is still reduced since sorption has reduced the aqueous concentration of the contaminant. When the intrinsic activity is faster than the release rates of the contaminant from soil, the release rates will be rate-limiting. It is usually believed, that the latter situation exists at contaminated sites [7].

The relation between desorption kinetics and degradation kinetics have been studied extensively in literature, see e.g. [7, 31, 34, 49, 55, 67, 73]. However, few studies exist that have tried to predict degradation in soil based on measured degradation kinetics in the absence of soil and measured desorption kinetics in absence of the micro-organisms. To be able to predict the possible success of bioremediation, the assumption that degradation in soil can be described when the desorption kinetics and the microbial activity are known needs to be validated. Such a study is presented in Chapter 5 of this thesis.

CHAPTER 2

Interactions between a Hydrophobic Organic Chemical and Natural Organic Matter: Equilibrium and Kinetic Studies*

Wendela Schlebaum, Aleksandra Badora, Gosse Schraa and Willem H. van Riemsdijk

ABSTRACT

Interactions between a well-characterised, purified, peat humic acid and pentachlorobenzene were studied in equilibrium and kinetic experiments. The kinetic experiments, performed with a gas-purge method, showed the presence of a fast desorbing, labile, fraction and a slow desorbing, non-labile, fraction. Increased contact time did not change the measured continuous desorption curves. A desorption experiment with interrupted flow and the measured isotherm suggested non-linear sorption behaviour. A first-order model consisting of two parallel "sites" could describe the continuous desorption curves but failed to describe the adsorption isotherm and the desorption curve with interrupted flow. A Langmuir model with one site was able to describe the characteristics of the desorption experiments and of the adsorption isotherm, but it did not describe the observed non-labile fraction. Expanding the model with an additional Langmuir or first-order site did not lead to a good description of the various experiments. We speculate that the non-labile fraction is a consequence of a change of conformation of the humic acid after the binding of pentachlorobenzene. This structural change leads to entrapment of pentachlorobenzene within the humic acid structure.

*Environmental Science & Technology 1998, 32, 2273-2277

INTRODUCTION

Remediation of polluted soils or sediments may be hindered by the binding of hydrophobic organic chemicals (HOCs) on or into the soil matrix. For risk evaluation of polluted soils, or to be able to predict the outcome of remediation projects, one should be able to describe the binding. Equilibrium partitioning expressions can be used to describe the binding when the time scale of transport and degradation is larger than the time scale of sorption. When equilibrium expressions are used, sorption is regarded to be instantaneous. However, sorption processes may have time scales of weeks or months, thus prescribing the use of kinetic expressions [62].

The release of HOCs from soils and sediments often shows biphasic desorption behaviour with a fast desorbing, labile, fraction and a slow desorbing, non-labile, fraction. The important role of organic matter in the overall binding is well established as demonstrated by the use of organic carbon normalised partition coefficients. However, only in recent literature the possible role of organic matter in slow sorption has received more attention. It is suggested that the labile fraction is composed of relatively open humic structures and the non-labile fraction is composed of more condensed, rigid humic structures [14, 39, 85].

Rigid humic structures may be formed by humin or kerogene-like materials [39], but also humic acids may have condensed and rigid regions [4, 62, 85, 87]. This implies that for rigid humic acid structures slow sorption kinetics can be observed. Only a few studies have been focused on the kinetics of interactions between humic substances and neutral HOC. McCarthy and Jimenez [48] and Hassett and Milicic [32] were unable to detect biphasic desorption for aqueous solutions of a commercial humic acid (Aldrich humic acid), but Aochi and Farmer [4] did detect biphasic sorption behaviour for 1,2-dichloroethane in the vapour state and dry soil humic acids. The latter study also demonstrated that slow sorption kinetics were correlated to the presence of rigid structures in the humic acids.

To investigate the interactions between a non-ionic hydrophobic organic pollutant (pentachlorobenzene) and organic matter in soils, we used a well-characterised peat humic acid [6, 51]. For the peat humic acid studied, a molecular weight of 23,000 has been given as an upper limit [51]. On the basis of proton titrations and this molecular weight, the radius of the humic acid particles has been determined to be between 2 and 4 nm, depending on the salt level [6]. Since pentachlorobenzene has a radius of 0.32 nm, we do not regard radial diffusion or intraorganic matter diffusion as a rate-limiting process for the interactions between pentachlorobenzene and peat humic acid. Sorption on or into rigid structures, however, may take place.

To get a better understanding of the kinetics of the interactions and the nature of the binding between pentachlorobenzene and peat humic acid, equilibrium and kinetic experiments were performed. The adsorption isotherm was measured in a batch system, while desorption kinetics were studied in a gas-purge system. Furthermore, desorption kinetics were measured continuously and in an experiment with interrupted flow. As the experiments differ in experimental set-up, they can be used to test the predictive capability of different models.

MATERIALS AND METHODS

Materials

Humic acids were prepared from "Irish Peat" following the extraction procedure of the International Humic Substances Society, as modified by Reid et al. [63]. Pentachlorobenzene (QCB, Merck, 98% pure) was used as the hydrophobic organic pollutant. The purified peat Humic Acids (ppHA) solutions for adsorption and desorption experiments had a concentration of $500\,\mathrm{mg\,l^{-1}}$, were set to pH = 5 and had a background-electrolyte concentration of 0.01 M $NaNO_3$. To ensure an equilibrium conformation of ppHA, all ppHA solutions were prepared 24 h before adsorption of QCB took place.

To determine the QCB concentration in humic and aqueous solutions, samples were extracted with hexane at room temperature for at least 24 h. QCB in the hexane phase was analysed with a Hewlett-Packard 5890 series II gas-chromatograph equipped with a HP 5 column and a Hewlett-Packard mass selective detector (series 5971) in selective ion monitoring mode.

The loading of an aqueous solution with or without humic acids was done via the gas phase at 20 °C. Air was pumped through a glass tube filled with pure QCB. The air with QCB in the vapour state was led through the aqueous solution under continuous stirring. Gas flow in the adsorption studies was approximately $70\,\mathrm{ml\,min^{-1}}$. In this way, a controlled loading of the humic acids was achieved.

Adsorption Isotherm

The equilibrium dialysis method [15] was used to determine the adsorption isotherm. A 5-ml sample of a ppHA solution ($500\,\mathrm{mg\,l^{-1}}$, pH 5, 0.01 M $NaNO_3$) was added to a dialysis bag (Spectra/Por 7, mol wt cutoff of 1000) and placed in a 125-ml glass jar containing 100 ml of an aqueous solution of QCB (pH 5, 0.01 M $NaNO_3$) at different concentrations. The jar was sealed with a Viton-lined cap and shaken (end-over-end) in the dark at 20 °C for 6 days. After 6 days, the QCB concentration was measured inside and outside the bag. In initial experiments, the time needed to reach

constant concentrations inside and outside the dialysis bag was determined to be less than 6 days.

Desorption Experiments

The gas-purge experimental set-up was based on the one used by Karickhoff and Morris [44]. The purge bottles, which had a diameter of 5 cm and a suspension volume of 100 ml, were thermostated at 20 °C. Experiments were done in triplicate as three bottles could be purged (parallel, with individual flow meters) at the same time. Some data sets consist of duplicates as a result of gas leakage in one of the three bottles. The solutions were purged with 500 ml min^{-1} nitrogen. QCB was trapped on columns with approximately 2 g Tenax (Tenax TA 60–80 mesh Chrompack, used as received). Tenax columns were extracted with 10 ml of hexane. In preliminary experiments, it was determined that 10 ml of hexane was sufficient for total extraction of QCB from the Tenax column. The hexane samples were concentrated under air after addition of an internal standard, 1,2,4,5-tetrachlorobenzene (Aldrich, 98% pure) in hexane, and analysed. At the end of a desorption experiment, the residual concentration was measured in 5-ml samples from the bottles (extracted with 1 ml of hexane). The initial total concentration for the desorption experiments was calculated by combining the amount recovered on the Tenax columns and the residual amount in the solution. The recoveries were 80–120%. A solution of QCB in water was purged to determine the rate with which the chemical is stripped from the water phase. The value obtained for the gas-purge rate constant, k_{gp} was 5.28 h^{-1}.

Desorption was followed continuously in ppHA solutions with a high and a low initial QCB concentration. Humic acid solutions with a high initial QCB concentration were obtained after an 8 day period of adsorption via the gas phase. After this adsorption period, adsorption via the gas phase was stopped, and desorption kinetics were measured either at day 0, after 2 days and after 29 days. The results from day 0 and day 29 were from the same adsorption batch. Half of it was used to measure desorption kinetics directly; the other half was set aside for 29 days at 10 °C in the dark, after which desorption kinetics were measured again. To measure the desorption kinetics of ppHA solutions with low initial QCB concentrations, concentrated humic acid solutions (pH 5, 0.01 M $NaNO_3$) were dissolved in an aqueous solution of QCB (pH 5, 0.01 M $NaNO_3$) resulting in the usual final ppHA concentration. These solutions were stored for 7 and 42 days at 20 °C. Both solutions were stirred in the first week. In none of the stored ppHA solutions were indications of microbial QCB degradation observed.

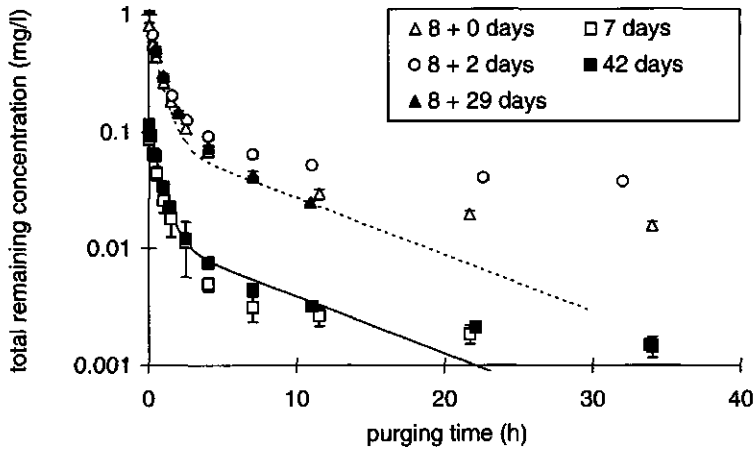

FIGURE 2.1. Continuous desorption of QCB from ppHA. Measured data are represented by symbols, error bars represent standard deviations but may fall within the symbol. Fitted (solid line) and predicted (dashed line) curves are obtained with first-order model. For curves with a low initial concentration ($\pm 0.1\,\mathrm{mg\,l^{-1}}$), the given times indicate the contact time between QCB and ppHA (7 or 42 days) prior to desorption. The closed squares experiment was fitted. For curves with a high initial concentration ($\pm 1.0\,\mathrm{mg\,l^{-1}}$), the given times indicate the duration of loading via the gas phase (8 days) plus the additional period between the end of the adsorption via the gas phase and the start of the desorption experiment (0, 2 or 29 days). The open triangles experiment was predicted.

The desorption experiment with interrupted flow started at a high initial QCB concentration. After an 8 day period of adsorption via the gas phase, the ppHA solution was transferred to gas-purge bottles and desorption was followed for 1.5 h. After 1.5 h, the purging was stopped and the bottles were closed with Teflon-lined caps. The bottles were then shaken (end-over-end) for 7 days at 20 °C, after which the purging was resumed and desorption was followed again.

RESULTS

Continuous desorption curves of ppHA solutions with high ($\pm 1\,\mathrm{mg\,l^{-1}}$) and low ($\pm 0.1\,\mathrm{mg\,l^{-1}}$) initial QCB concentrations are shown in Figure 2.1. High initial QCB concentrations were obtained by pumping air with QCB in the vapour state through an aqueous solution of ppHA. To investigate

the effect of contact time between QCB and ppHA, desorption started either 0, 2 or 29 days after the end of the adsorption via the gas phase (high initial QCB concentrations) or 7 or 42 days after dissolving a ppHA solution in an aqueous solution of QCB (low initial QCB concentrations). The increased contact time between QCB and ppHA does not result in slower desorption. This implies that, for both the high and the low initial QCB concentrations, equilibrium binding is reached before the desorption experiment starts. Furthermore, the curves with a low and high initial concentration are remarkably similar. If, for all curves, the remaining concentrations (y-axis) are normalised to their initial concentrations, the low initial QCB concentration curves fall in between the curves with a high initial concentration. Assuming that equilibrium has indeed been reached at the start of the experiments, it indicates that the desorption rate is independent of the total *initial* concentration. This is a typical characteristic of first-order kinetics which is based on linear sorption or partitioning.

Although desorption of the majority of QCB is fast (within 3–5 h), the desorption curves do show biphasic desorption, suggesting the existence of a slow desorbing fraction. The residual concentration is 1.3–3.7% of the total initial concentration. The slow desorbing fraction is not the result of insufficient purging, since it is not influenced by the QCB concentration in the aqueous phase.

The results of the desorption experiment in which the purging was interrupted for a period of 7 days are shown in Figure 2.2. The temporary stop of the purging does not result in a visible discontinuity of the predicted desorption curve. No redistribution of QCB from the non-labile fraction to the labile fraction is visible after one week rest. This implies that either the rate constants are so small that no significant redistribution occurs during the period that no purging took place or that the system is very close to, or at, equilibrium when the purging stops. The latter is possible when the sorption behaviour is non-linear.

The adsorption isotherm of QCB and ppHA, measured with the dialysis method, and the calculated partition coefficient are shown in Figure 2.3. The measured isotherm levels off above an aqueous concentration of $0.1\,\mathrm{mg\,l^{-1}}$, indicating non-linear sorption behaviour. The partition coefficient of QCB and ppHA was calculated by measuring the maximum total concentration of QCB in aqueous and humic acid solutions after the loading of the solutions with QCB. If equilibrium is reached and maximum binding is achieved, the concentration in the water phase (C_{aq}) is equal to the solubility of QCB. The measured solubility of QCB in water was $0.30 \pm 0.02\,\mathrm{mg\,l^{-1}}$ and the apparent solubility in the humic acid solution was

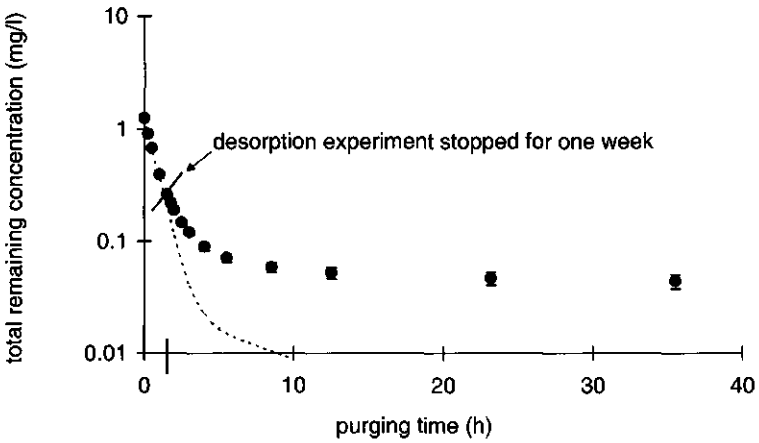

FIGURE 2.2. Desorption of QCB from ppHA with interrupted flow. Measured data are represented by symbols, error bars represent standard deviations but may fall within the symbol. Predicted (dashed line) curve is obtained with first-order model. The moment at which the purging is interrupted is indicated in the curve and on the x-axis. Note that the x-axis is continuous, indicating total purging time.

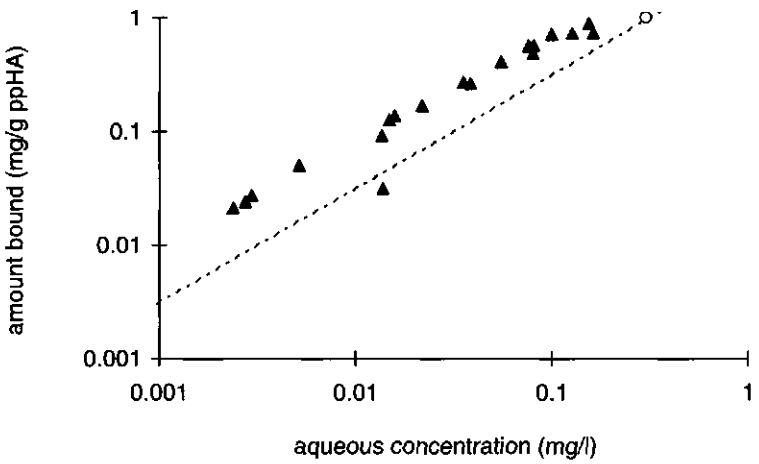

FIGURE 2.3. Adsorption isotherm. Measured data are represented by symbols. Predicted (dashed line) curve is obtained with first-order model. The partition coefficient, as calculated from maximum loading via the gas phase, is also given (open circle).

$0.81 \pm 0.07\,\mathrm{mg\,l^{-1}}$, which resulted in a bound concentration of $0.51\,\mathrm{mg\,l^{-1}}$. This had been measured in experiments that lasted 20 days, and in which equilibrium seemed to be reached after 7 days (data not shown). With an organic carbon (OC) content of approximately 50%, this gives an OC-normalised partition coefficient (K_{OC}) of 6800, or a log K_{OC} of 3.8. This value is comparable to values reported in literature for soils and sediments [11].

MODELLING DESORPTION KINETICS

Two models were tested to describe the interactions between QCB and ppHA, a first-order kinetic model and a kinetic model based on Langmuir sorption. A first-order model, which is based on a linear sorption isotherm, was tested since the desorption rate of the continuous desorption curves is independent of the total initial concentration. As both the adsorption isotherm and the desorption curve with interrupted flow seem to suggest non-linear sorption, the second kinetic model tested is based on Langmuir sorption.

Different first-order models have been used in literature to describe desorption from soils or sediments [9, 18, 21, 44, 61]. The most often used model is the two-compartment model with two "sites" in series [9, 44, 61]. This model is usually related to diffusion into particles, which we do not regard as a rate-limiting process for the interactions between QCB and ppHA. It is usually assumed that the two compartments differ only in kinetics and not in their affinity for the HOC [9, 44]. The model used in this study is a parallel model with two discrete sites that may have different affinities for HOC and different sorption kinetics. Such a model may correspond to sorption on or into different humic structures that vary in hydrophobicity or rigidness. The equations defining the model are as follows, for $i = 1, 2$:

$$q_i = K_{\mathrm{p},i} C_{\mathrm{aq}}, \tag{2.1}$$

$$\frac{dq_i S}{dt} = -k_{\mathrm{d},i} q_i S + k_{\mathrm{a},i}^{\mathrm{app}} C_{\mathrm{aq}}, \tag{2.2}$$

$$\frac{dC_{\mathrm{aq}}}{dt} = \sum_{i=1}^{2} k_{\mathrm{d},i} q_i S - \sum_{i=1}^{2} k_{\mathrm{a},i}^{\mathrm{app}} C_{\mathrm{aq}} - k_{\mathrm{gp}} C_{\mathrm{aq}}, \tag{2.3}$$

where q_i is the amount of QCB bound (mg of QCB (kg of ppHA)$^{-1}$) to site i; C_{aq} ($\mathrm{mg\,l^{-1}}$) is the aqueous concentration of QCB; $K_{\mathrm{p},i}$ ($\mathrm{l\,kg^{-1}}$) is the partition coefficient for site i; $k_{\mathrm{d},i}$ ($\mathrm{h^{-1}}$) and $k_{\mathrm{a},i}^{\mathrm{app}}$ ($\mathrm{h^{-1}}$) are the desorption and adsorption rate constant; k_{gp} ($\mathrm{h^{-1}}$) is the gas-purge rate constant, and

S ($\mathrm{kg\,l^{-1}}$) is the sorbent concentration. Equations 2.1 and 2.2 are correlated since at equilibrium $dq_i S/dt = 0$, which gives $K_{\mathrm{p},i} = k_{\mathrm{a},i}^{\mathrm{app}}/(k_{\mathrm{d},i}S)$. As it is virtually impossible to determine the actual size of each site, the amount sorbed to each site is expressed as milligram per kilogram of sorbent instead of milligram per kilogram of site i. Note that it is necessary to use the amount of QCB bound (q_i) times the sorbent concentration (S) to be able to relate the amount bound to the concentration in the water phase (eqs. 2.2 and 2.3). As the above equations imply that the adsorption rate constant is linear with the sorbent concentration, it is an apparent $k_{\mathrm{a},i}$. As the concentration of site i is unknown, the apparent adsorption rate constant ($k_{\mathrm{a},i}^{\mathrm{app}}$) may be normalised by the total amount of sorbent present (S).

The Langmuir model may correspond to sorption on or into specific ppHA structures or holes [85]. The equations defining a kinetic model based on Langmuir sorption behaviour are

$$q = \frac{q_{\max} K C_{\mathrm{aq}}}{1 + K C_{\mathrm{aq}}}, \tag{2.4}$$

$$\frac{dqS}{dt} = -k_{\mathrm{d}} q S + k_{\mathrm{a}}^{\mathrm{app}} C_{\mathrm{aq}} \left(q_{\max} S - qS\right), \tag{2.5}$$

$$\frac{dC_{\mathrm{aq}}}{dt} = k_{\mathrm{d}} q S - k_{\mathrm{a}}^{\mathrm{app}} C_{\mathrm{aq}} \left(q_{\max} S - qS\right) - k_{\mathrm{gp}} C_{\mathrm{aq}}, \tag{2.6}$$

where $q_{\max}$ ($\mathrm{mg\,kg^{-1}}$) is the capacity of the Langmuir site, K ($\mathrm{l\,mg^{-1}}$) is the Langmuir binding coefficient and $k_{\mathrm{a}}^{\mathrm{app}}$ ($\mathrm{l\,mg^{-1}\,h^{-1}}$) is the apparent adsorption rate constant. The other symbols are as defined above (as only one site is present the subscript i is removed).

Starting from an initial guess, the unknown parameters for both models were fitted to the experimental data using a least-squares criterion and a Newton-Raphson method. Each iteration step involved numeric integration of the set differential equations. We used a standard fourth-order Runge-Kutta method for this purpose. The initial condition for the desorption curves is dependent on the adsorption method. For the curves with a low initial QCB concentration, adsorption occurred via the water phase and for a known adsorption period. Therefore, the amount bound to the two sites at the start of the desorption period can easily be calculated with the parameters that are fitted to the desorption curve. For the high initial QCB concentrations, an additional factor would have to be introduced to describe the adsorption via the gas phase. Since increased contact time did not result in lower desorption rates, equilibrium binding at the start of the desorption was assumed for the desorption curves with a high initial QCB concentration.

TABLE 2.1. Parameters Obtained from the Fit with the First-Order Model and with the Langmuir Model[a]

First-Order		Langmuir	
$k_{a,1}^{app}$ (h^{-1})	4.02	k_a^{app} ($l\,mg^{-1}\,h^{-1}$)	4.55
$k_{d,1}$ (h^{-1})	2.98	k_d (h^{-1})	1.66
$k_{a,2}^{app}$ (h^{-1})	2.71×10^{-2}	q_{max} ($mg\,kg^{-1}$)	2.74×10^3
$k_{d,2}$ (h^{-1})	1.13×10^{-1}	K ($l\,mg^{-1}$)	2.75
$K_{p,1}$ ($l\,kg^{-1}$)	2.69×10^3		
$K_{p,2}$ ($l\,kg^{-1}$)	4.82×10^2		

[a] For the first-order model, the continuous desorption curve with a low initial concentration and an adsorption period of 42 days was fitted. For the Langmuir model, desorption with interrupted flow and the isotherm were fitted simultaneously.

The validity of the first-order kinetics model was tested by fitting it to a continuous desorption curve with a low initial QCB concentration. The fitted parameters were then used to predict (1) continuous desorption with a high initial QCB concentration, (2) the measured adsorption isotherm, and (3) desorption with interrupted flow. These results are shown in Figures 2.1, 2.2, and 2.3. The values for the parameters, obtained from the fitted data and used for the predicted curves, are given in Table 2.1. The fit of the continuous desorption curve with a low initial QCB concentration and an adsorption period of 42 days and the predicted high initial QCB concentration curve measured directly after the loading with QCB via the gas phase are given in Figure 2.1. The fitted and predicted desorption curve are identical after normalising the remaining concentration (y-axis) to the total initial concentration. The fit indicates that, for adsorption via the water phase, equilibrium is reached within one week (data not shown). This justifies our assumption that, for all the continuous desorption experiments, equilibrium was reached before desorption started. The model fails to describe the last data points, suggesting the presence of an additional site or even a distribution of sites. However, since only the last two data points are not described, these data are insufficient to justify the addition of another site to the model.

The prediction of the desorption experiment with interrupted flow (Figure 2.2) follows the data closely until the data point at 1.5 h where the purging was temporarily stopped. The temporary stop of the purging results in a visible discontinuity of the predicted desorption curve. The predicted desorption rate is increased after the purging is resumed. The increase of

the desorption rate is due to redistribution of QCB from the non-labile fraction to the labile fraction during the period that no purging took place. This calculated effect is clearly at variance with the experimental data.

The measured and predicted adsorption isotherms are given in Figure 2.3. The prediction underestimates the adsorption for almost the complete concentration range. The partition coefficient, which was calculated for maximum loading via the gas phase, is described well, although the data to which the model was fitted were below this concentration.

The Langmuir model was tested by fitting it simultaneously to the adsorption isotherm and to the desorption curve with interrupted flow. The continuous desorption curves were then predicted with the obtained parameters. The results obtained with the Langmuir model are given in Figure 2.4, and the values for the parameters, obtained from the fitted data and used for the predicted curves, are given in Table 2.1. The description of the adsorption isotherm is good (Figure 2.4C). Furthermore, the fact that the temporary stop of the purging does not result in a visible discontinuity of the desorption curve is now also well described (Figure 2.4B). The model description indicates that a slight redistribution of QCB occurs until 1.5 h after the end of the first desorption period. After the purging is resumed, the fitted curve follows the data closely for another hour. The tail of the desorption curve with interrupted flow cannot be described.

The measured and predicted continuous desorption curves are given in Figure 2.4A. The desorption curve with a high initial concentration can be described reasonably well for the initial 90% removed. For the desorption curve with a low initial concentration, the predicted desorption in the initial stage is less well described since the model underestimates the observed initial desorption rate. This is an intrinsic characteristic of the Langmuir model since Langmuir sorption implies that relatively more QCB is bound at lower concentrations, which will lead to lower desorption rates.

DISCUSSION

Compared to the first-order model, the Langmuir model gives a better description of the adsorption isotherm, the desorption experiment with interrupted flow, and the continuous desorption experiments. For a better description of the tail of the desorption curves, the Langmuir model has to be expanded. Although a model with two Langmuir sites is rather flexible with six fitting parameters, simulations (not shown) have indicated that this model cannot describe the complete set of data. To describe the non-labile fraction, a Langmuir site with a high affinity (K) and small desorption rate constant (k_d) is needed. A high affinity will increase the relative amount

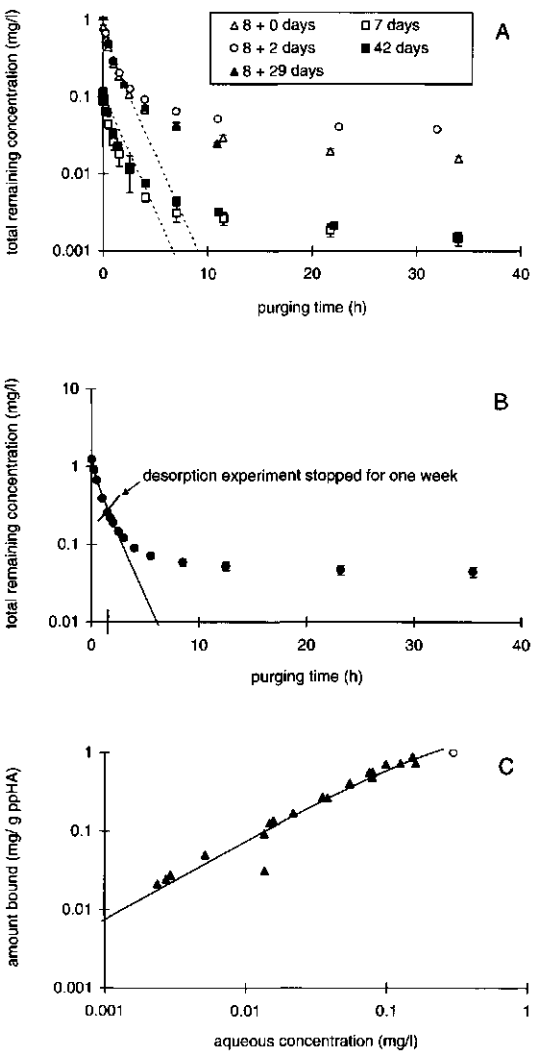

FIGURE 2.4. Fitted (solid line) and predicted (dashed line) curves obtained with Langmuir model. Measured data are represented by symbols and are also given and described in Figures 2.1, 2.2, and 2.3. (A) Continuous desorption of QCB from ppHA. The open triangles and closed squares experiments are predicted. (B) Desorption of QCB from ppHA with interrupted flow. (C) Adsorption isotherm.

of QCB bound to the non-labile faction at low initial QCB concentrations compared to high initial QCB concentrations. This results in significantly lower desorption rates for the curves with a low initial concentration, which has not been observed experimentally. A small desorption rate constant and a moderate affinity will result in a small adsorption rate constant. With a small adsorption rate constant, increased contact time will increase the amount bound to the non-labile fraction with a concomitant decrease of the desorption rates. This has also not been observed experimentally. In the Langmuir model with one site, this effect was small due to the relatively low affinity and large desorption rate constant of this site.

A model with a linear site to describe the labile fraction and a Langmuir site to describe the non-labile fraction, has been used by Xing and Pignatello [85] and Huang et al. [40]. However, a fast adsorbing and desorbing linear site will lead to redistribution of QCB during the stop in the desorption experiment with interrupted flow. This was not observed in our experiments. Furthermore, as discussed above, the non-labile fraction in the continuous desorption experiments could not be described with a Langmuir term.

As increased contact time did not result in lower desorption rates, slow adsorption or diffusion processes into rigid structures do not seem to occur for the interactions between QCB and ppHA. The biphasic desorption curves, however, suggest the presence of a slow desorbing fraction. The occupancy of this fraction increases linearly with the total amount initially sorbed. We could not find a model able to describe all our data. Although it may be very speculative, our results do show some similarity with the data from Kan et al. [43]. They studied sorption kinetics of naphthalene to sediment and surrogate sediments in experiments consisting of several successive adsorption/desorption steps. Part of the amount sorbed seemed to resist desorption but could be extracted with an organic solvent and was defined to be "irreversibly" bound. The amount bound to this fraction increased proportionally to the initial naphthalene concentration. The term irreversible was used to imply that there is a rearrangement of the solid or organic carbon matrix in an irreversible manner and that desorption from this altered matrix is not the reverse of the adsorption process. In our study, the residual concentration is also proportional to the initial concentration. Furthermore, part of the amount sorbed resists desorption. The latter was clearly visible in the desorption experiment with interrupted flow. For humic acids, a change of the three-dimensional structure after adsorption of a pollutant may occur. This change of conformation may well lead to entrapment of QCB. For ppHA and QCB, the change occurs relatively fast

since slow adsorption was not observed. Irreversible sorption or entrapment of QCB in the ppHA structure is not likely to be described with simple equations. Furthermore, these phenomena are easily overlooked with most experimental methods. If only continuous desorption curves would have been measured, the non-linear nature of the binding of QCB to ppHA would not have been detected. Our experiments demonstrate that the interactions between HOC and natural organic matter in soils or even purified humic acids are not yet fully understood. However, it is clear that simple linear sorption or partitioning is not able to describe the interactions between QCB and humic acid.

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CHAPTER 3

Influence of Non-Linear Kinetics on the Slow Desorbing Organic Contaminant Fraction in Soil*

Wendela Schlebaum, Gosse Schraa, Willem H. van Riemsdijk

ABSTRACT

Release rates of hydrophobic organic compounds (HOCs) from the soil matrix influence the availability of HOCs in soils or sediments for microbial degradation or removal by physical means (e.g. soil washing or soil venting). In this study it was shown that the initial contaminant concentration influenced the desorption rate. This was attributed to the presence of a limited number of high affinity sites that cause non-linear sorption behaviour. The experimental results could be described with a kinetic model composed of two separate compartments. One compartment was described with a Freundlich isotherm and corresponding kinetics and was assumed to represent sorption to high affinity sites. The second compartment was described with a linear sorption isotherm and first-order kinetics. The model was used to simulate the influence of purging strategies on removal of QCB. The simulations showed that after removal of a fast desorbing fraction, the slow desorbing fraction could be efficiently removed at very slow purging rates. Intermittent purging reduced the total purging time but the simulations showed large fluctuations in the aqueous pentachlorobenzene concentration. For each subsequent purging interval, the purging efficiency decreased due to the non-linear sorption behaviour of the slow desorbing fraction of pentachlorobenzene.

*submitted

INTRODUCTION

The availability of hydrophobic organic compounds (HOCs) in soils or sediments for microbial degradation or removal by physical means (e.g. soil washing or soil venting) depends on the release rate of HOCs from the soil matrix. When HOCs are released very slowly from the soil matrix, remediation of polluted sites may be hampered. Knowledge of factors influencing the magnitude and kinetics of the slow desorbing fraction is a prerequisite for the development of models that can be used to simulate the outcome of remediation projects.

Diffusion of HOC in the heterogeneous soil matrix, occurring in either mineral pores or in organic matter, is generally accepted to play a role in slow desorption kinetics of HOC. However, diffusion models with a constant diffusion coefficient cannot describe several features of the sorption behaviour of HOCs in soils [62]. These features include an inverse correlation between the magnitude of the slow desorbing fraction and the initial HOC concentration, see refs. in [62]. This and measured non-linear sorption isotherms [16, 29, 39, 40, 85] suggest that a limited number of sites exist that exhibit high sorption energies [16, 62]. Chiou and Kile [16] found that at high HOC concentrations sorption isotherms became linear and they attributed this to a partitioning process. Sites with a high sorption energy were postulated to result from adsorption of HOC to charcoal-like substances [16]. Huang and Weber [39] also demonstrated that geologically older soil samples with more physically condensed and chemically reduced soil organic matter showed higher affinities and increasing non-linear sorption behaviour.

Non-linear sorption isotherms will influence diffusive processes since the non-linearity will result in concentration-dependent diffusion coefficients [20]. In case of a Freundlich sorption isotherm with a Freundlich exponent < 1, the effective diffusion coefficient increases with increasing solute concentration [20]. This indicates that equilibrium is reached faster at high HOC concentrations than at low HOC concentrations. Apart from effects on adsorption rates, non-linear sorption also results in slower desorption than adsorption. For non-linear sorption, especially the last stages of desorption are extremely slow [20].

We have investigated the effects of loading history and contact time on the desorption kinetics of the slow desorbing fraction. Soil suspensions were either loaded via the gas phase, which resulted in a high initial HOC concentration, or soil samples were suspended in an aqueous solution of HOC at a low concentration. The kinetics of the slow desorbing fraction were investigated more closely by following desorption kinetics in two subsequent

periods with an intermittent period to allow for redistribution of HOC from the slow desorbing compartment to a fast desorbing compartment. The influence of different purging strategies on the removal of the slow desorbing fraction and the subsequent change of pentachlorobenzene concentration in the aqueous phase was studied in simulations with a kinetic model that was able to describe the complete set of data.

KINETIC MODEL

The objective of the kinetic model is to investigate the influence of non-linear sorption on removal of HOC from soil by simulating the influence of different purging strategies. The model should therefore be able to describe all the data and it should account for the influence of a limited number of high affinity sites in combination with a partitioning process. To calibrate the model, experimental data are needed that clearly show the influence of non-linear kinetics. As discussed before, data in the literature concerning sorption of HOCs to soil suggest that intraparticle or intraorganic matter diffusion models using linear sorption isotherms cannot explain the observed phenomena [62]. A limited number of high affinity sites leads to a non-linear sorption isotherm and perhaps also to slow desorption kinetics.

For intraparticle and intraorganic matter diffusion models with high affinity sites, assumptions have to be made regarding the shape, size and size distribution of the particles (e.g. spheres with certain radii); pore geometry; diffusion coefficient; and number, nature and spatial distribution of the high affinity sites in the particles. These characteristics are at present not measurable. The assumptions mentioned above can be circumvented by using a model with rate coefficients. Although the rate coefficients may not have an a priori physical significance [59], these models can be very useful for simulations. Kinetic models based on first-order or non-linear rate coefficients have been shown to be able to give in some cases an equally good description of measured sorption kinetics compared to diffusion models [50, 59, 82]. When diffusion kinetics are rapid compared to sorption kinetics, which is possible for the high energy sites, sorption kinetics will be the rate-controlling process [20].

In this study, high affinity sites were described by a compartment with a Freundlich sorption isotherm and corresponding n^{th}-order kinetics. Partitioning or adsorption to mineral surfaces was described by a separate second compartment characterised by a linear sorption isotherm and first-order kinetics. Although the Freundlich isotherm was initially developed as an empirical equation, it is now known that the Freundlich exponent n can

be interpreted as a measure of the heterogeneity of a sorbent. A Freundlich isotherm has been shown to be equal to an isotherm that consists of multiple Langmuir isotherms, see e.g. [81]. The sorption isotherms for the slow desorbing and fast desorbing compartment are given by the following equations:

$$q_{\mathrm{f}} = K_{\mathrm{f}} C_{\mathrm{aq}}^{n}, \tag{3.1}$$

$$q_{\mathrm{l}} = K_{\mathrm{l}} C_{\mathrm{aq}}, \tag{3.2}$$

where q_{f} and q_{l} ($\mathrm{mg\,kg^{-1}}$) are the amount of pollutant bound to the Freundlich and linear compartment respectively; K_{f} ($(\mathrm{mg\,kg^{-1}})(\mathrm{mg\,l^{-1}})^{-n}$) is the Freundlich binding coefficient; K_{l} ($\mathrm{l\,kg^{-1}}$) is the linear partition coefficient; n is the Freundlich exponent which is a measure of the chemical heterogeneity, and C_{aq} ($\mathrm{mg\,l^{-1}}$) is the aqueous concentration. The equations used to describe the kinetics of the interactions are:

$$\frac{dq_{\mathrm{f}}S}{dt} = -k_{\mathrm{d,f}} q_{\mathrm{f}} S + k_{\mathrm{a,f}}^{\mathrm{app}} C_{\mathrm{aq}}^{n}, \tag{3.3}$$

$$\frac{dq_{\mathrm{l}}S}{dt} = -k_{\mathrm{d,l}} q_{\mathrm{l}} S + k_{\mathrm{a,l}}^{\mathrm{app}} C_{\mathrm{aq}}, \tag{3.4}$$

$$\frac{dC_{\mathrm{aq}}}{dt} = k_{\mathrm{d,f}} q_{\mathrm{f}} S + k_{\mathrm{d,l}} q_{\mathrm{l}} S - k_{\mathrm{a,f}}^{\mathrm{app}} C_{\mathrm{aq}}^{n} - k_{\mathrm{a,l}}^{\mathrm{app}} C_{\mathrm{aq}} - k_{\mathrm{gp}} C_{\mathrm{aq}}, \tag{3.5}$$

where $k_{\mathrm{d,f}}$ ($\mathrm{h^{-1}}$) and $k_{\mathrm{a,f}}^{\mathrm{app}}$ ($(\mathrm{mg\,l^{-1}})(\mathrm{mg\,l^{-1}})^{-n})\,\mathrm{h^{-1}}$) are the desorption and apparent adsorption rate constant of the Freundlich compartment; $k_{\mathrm{d,l}}$ ($\mathrm{h^{-1}}$) and $k_{\mathrm{a,l}}^{\mathrm{app}}$ ($\mathrm{h^{-1}}$) are the desorption and apparent adsorption rate constant of the linear compartment; k_{gp} ($\mathrm{h^{-1}}$) is the gas-purge rate constant, and S ($\mathrm{kg\,l^{-1}}$) is the sorbent concentration. The sorption isotherms of the Freundlich and linear compartment (eqs. 3.1 and 3.2) can be found since at equilibrium $dqS/dt = 0$, and solving equations 3.3 and 3.4 shows that the binding coefficients are a function of the rate coefficients. Note that it is necessary to use the amount of QCB bound (q) times the sorbent concentration (S) to be able to relate the amount bound to the concentration in the water phase (eqs. 3.3, 3.4, and 3.5). In the above equations, the adsorption rate constants are linear with the sorbent concentration and they are therefore apparent adsorption rates. To obtain the normalised adsorption rate constant (k_{a}) the apparent adsorption rate can be divided by the sorbent concentration.

MATERIALS AND METHODS

Materials and Solution Preparation

The soil used, Wageningen Eng soil, is a sandy soil which was air-dried and sieved. The sieve fraction used in this study was < 0.5 mm with an organic carbon content of 2.1%. Soil suspensions in the experiments had an organic carbon content of $0.25\,g\,l^{-1}$ ($12.2\,g\,soil\,l^{-1}$), final pH after equilibration was pH 5 (obtained after addition of HCl), 0.01 M $NaNO_3$ was added as background electrolyte and 0.1 mM NaN_3 was added to prevent microbial growth.

Pentachlorobenzene (QCB, Merck, 98% pure) was used as hydrophobic organic compound. The loading of soil suspensions or aqueous solutions with QCB was done via the gas phase at 20 °C. Air was pumped through a glass tube filled with pure QCB. The air with QCB in the vapour state was led through the soil suspension or aqueous solution under continuous stirring. Gas flow in the adsorption studies was approximately $70\,ml\,min^{-1}$. The aqueous solubility of QCB was determined to be $0.30\,mg\,l^{-1}$ with this method [69]. The measured total (sorbed + aqueous) QCB concentration in the soil suspensions did not change after 8 days loading via the gas phase and until the end of the loading period of 28 days.

Desorption Experiments

Desorption kinetics were followed in gas-purge experiments based on the method used by Karickhoff and Morris [44]. Details of the experiments are described elsewhere [69]. Desorption experiments were done in triplicate since three identical soil suspensions (100 ml) were purged simultaneously with nitrogen at 20 °C. QCB was trapped on Tenax columns. Hexane extracts of Tenax columns were concentrated, if necessary, under air after addition of an internal standard, 1,2,4,5-tetrachlorobenzene (Aldrich, 98% pure) in hexane. At the end of a desorption experiment at least 80 ml of the soil suspension was transferred to 4–5 extraction tubes. A solution of QCB in water was purged to determine the rate with which the chemical is stripped from the water phase. The value obtained for the gas-purge rate constant (k_{gp}) was $5.28\,h^{-1}$.

Desorption was followed continuously in soil suspensions with a high and a low initial QCB concentration. A soil suspension with a high initial QCB concentration was obtained after 28 days of adsorption via the gas phase. After this period, adsorption via the gas phase was stopped and half of the soil suspension was used to follow desorption kinetics directly; the other half was set aside for 42 days at 20 °C in the dark after which desorption kinetics were followed again. A soil suspension with a low initial

QCB concentration was obtained by adding the appropriate amount of soil to an aqueous solution of QCB (pH 5, 0.01 M $NaNO_3$, 0.1 mM NaN_3). The suspension was stored at 20 °C in the dark and stirred for 28 days. After this period, half of the soil suspension was used to follow desorption kinetics directly; the other half was set aside without stirring for another 42 days after which desorption kinetics were followed again. Soil suspensions were not stirred in this period since it was expected that after 28 days, the relevant adsorption process would be redistribution from the fast desorbing compartment to the slow desorbing compartment and that the aqueous concentration would remain virtually constant.

The desorption experiment with interrupted flow started with a soil suspension with a high initial QCB concentration. After 28 days of adsorption via the gas phase, the soil suspension was transferred to gas-purge bottles and desorption was followed for 48 hours. After 48 hours, the purging was stopped and the bottles were closed with Teflon-lined caps. The bottles were then shaken (end-over-end) for 28 days at 20 °C, after which the purging was resumed and desorption was followed again.

The total (sorbed + aqueous) initial QCB concentration for the desorption experiments was calculated by combining the amount recovered on the Tenax columns and the residual amount in the suspension. For all desorption experiments, the recoveries (ratio between the calculated and the measured total initial QCB concentration) were 90–100%. The recoveries of the desorption experiments were based on measured total initial QCB concentrations since the added amount of QCB could not be determined for the soil suspensions that were loaded via the gas phase. The use of measured total initial QCB concentrations further avoided the introduction of errors in the total initial QCB concentration due to losses via adsorption to glass walls or via volatilisation. When prolonged contact time causes a significant loss of QCB, the total initial QCB concentration of the desorption curve is affected and this will be revealed when the desorption curves of experiments with short and long contact times are compared.

Extraction and Analysis

To determine the QCB concentration, soil suspensions were shaken for a minimum of 5 days with hexane. The efficiency of the hexane extraction was tested by comparing total concentrations measured with the hexane extraction and measured after refluxing 50 ml of a soil suspension with 50 ml of hexane and 10 ml of acetone for 24 hours. The efficiency of the hexane extraction compared to the reflux extraction for the determination

of total initial QCB concentration in the soil suspensions was high: 95–105%, for both high and low initial QCB concentrations and independent of contact times of 28 or 70 days and even of 150 days. The efficiency of the hexane extraction for the determination of the residual concentration in the desorption experiments was tested in the desorption experiment with interrupted flow. In this case, the efficiency of the hexane extraction compared to the reflux extraction was 83%. The amount of QCB which is desorbed less readily is also extracted less readily. The good efficiency of the hexane extraction reflects domination of results by fast desorbing QCB even after 150 days but inefficiencies do exist for the slow desorbing fraction, evident only after "labile" QCB has been removed. For soils contaminated in the field hexane extractions have been observed to give poor recoveries [62]. The difference in residual QCB concentration between the hexane extraction and the reflux extraction was less than 1% of the initial concentration. The introduced error may result in an underestimation of the slow desorbing fraction. QCB in the hexane phase was analysed with a Hewlett-Packard 5890 series II gas-chromatograph equipped with a HP 5 column and a Hewlett-Packard mass selective detector (series 5971) in selective ion monitoring mode.

Data Analysis

Starting from an initial guess, the unknown parameters were fitted to the experimental data using a least-squares criterion and a Newton-Raphson method. Each iteration step involved numeric integration of the set of differential equations. We used a standard fourth order Runge-Kutta method for this purpose. The initial condition for the desorption curves is dependent on the adsorption method. For the curves with a low initial QCB concentration, adsorption occurred via the water phase and for a known adsorption period. Therefore, the amount bound to the two compartments at the start of the desorption period can easily be calculated with the parameters, the four rate constants and the Freundlich exponent n, that are fitted to the desorption curve. For the high initial QCB concentrations, an additional factor would have to be introduced to describe the adsorption via the gas phase. This factor could not be determined experimentally for the loading via the gas phase. When equilibrium binding may be assumed at the start of the desorption, the initial amount bound to each compartment can be calculated for the desorption curves with a high initial QCB concentration. To ensure that equilibrium could be reached, loading via the gas-phase was continued until 28 days while measured total concentrations were already constant after 8 days. To be able to fit a curve

with a high initial concentration, the aqueous QCB concentration at the start of the desorption experiments had to be used as additional parameter in the fit. This increased the number of parameters to be fitted to six for curves with a high initial QCB concentration. To test the fitting results, one desorption curve with a low and one desorption curve with a high initial QCB concentration were fitted simultaneously while the other curves were predicted with the obtained parameters.

RESULTS AND DISCUSSION

Influence of Contact Time and Initial Concentration

The effect of increased contact time on the magnitude of the slow desorbing fraction was investigated for a soil suspension with a high initial QCB concentration, as obtained after loading via the gas phase, and for a soil suspension where the soil was added to an aqueous solution of QCB. The latter resulted in a low initial QCB concentration and a low driving force for mass-transfer. Continuous desorption curves for the soil suspensions with a high initial concentration were measured either directly or 42 days after the end of the loading via the gas phase and are shown in Figure 3.1A. The results of the continuous desorption curves from the soil suspension with a low initial QCB concentration that were measured after 28 and 70 days total contact time are given in Figure 3.1B.

Figure 3.1A shows that increased contact time did not affect the desorption kinetics significantly of the soil suspensions with a high initial QCB concentration. After the period of loading via the gas phase, the magnitude of the slow desorbing fraction appeared to be independent of contact time. However, increased contact time did result in significantly slower desorption rates and a subsequent larger slow desorbing fraction for the soil suspension with a low initial QCB concentration (Figure 3.1B). These experiments show that at the start of the desorption experiments with a low initial QCB concentration, equilibrium was not yet reached while at high initial concentrations, equilibrium appeared to be reached. This is in accord with a non-linear sorption process, as discussed before.

Desorption with Interrupted Flow

The desorption experiment in which the purging was interrupted for a period of 28 days, is shown in Figure 3.2. After loading with QCB via the gas phase for 28 days, the first purging period started. During this period, a fast desorbing fraction of QCB could be removed in 48 hours of purging. After removal of the fast desorbing fraction, the suspension was set aside for 28 days. The second purging period started after these 28 days. At the

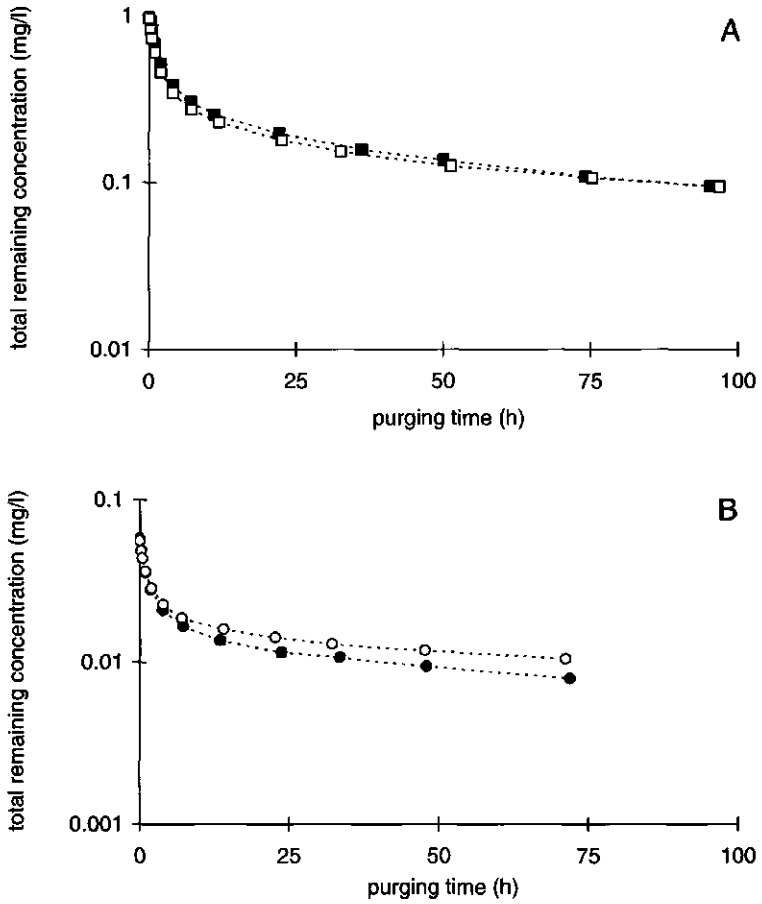

FIGURE 3.1. Continuous desorption of QCB from Wageningen Eng soil. The y-axis represents sorbed plus aqueous QCB concentration expressed in $\mathrm{mg\,l^{-1}}$. (A) Curves with a high initial concentration ($\pm 1\,\mathrm{mg\,l^{-1}}$) either measured directly (closed squares) or 42 days (open squares) after loading via the gas phase for 28 days. (B) Curves with a low initial concentration ($\pm 0.1\,\mathrm{mg\,l^{-1}}$) measured after 28 (closed circles) and 70 (open circles) days total contact time. Error bars represent standard deviations but may be obscured by the symbol.

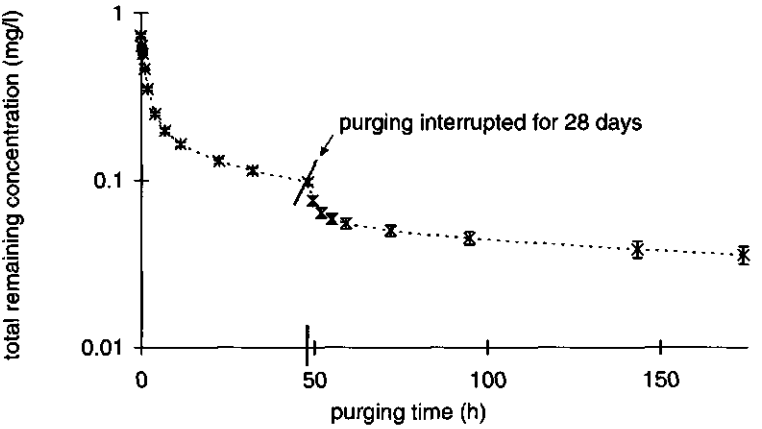

FIGURE 3.2. Desorption of QCB from Wageningen Eng soil with interrupted flow; the moment at which the purging was interrupted for 28 days is indicated on the curve and on the x-axis. Note that the x-axis is continuous, indicating total purging time. Error bars represent standard deviations but may be obscured by the symbol.

end of the first period, desorption rates were slow and all remaining QCB seemed to be bound to the slow desorbing compartment. After 28 days without purging, the desorption showed again a fast and a slow desorbing fraction. This is caused by redistribution of QCB from the slow desorbing compartment to the fast desorbing compartment. However, compared to the first period, the fast desorbing fraction of the second period was small and the slow desorbing fraction was increased. Farrell and Reinhard [25] also demonstrated in experiments with sediments, soil and a non-ionic organic contaminant that the slow desorbing contaminant fraction increased after an initial purging period and a subsequent re-equilibration period. Since the initial adsorption period and the period without purging were both 4 weeks, re-equilibration is obviously slower than the initial equilibration. This corresponds with non-linear sorption behaviour which implies that at high initial contaminant concentrations equilibrium sorption is reached faster than at low initial concentrations. The results indicate that large driving forces for mass-transfer can give rise to large fractions of slow desorbing HOC in a relatively short period. This has implications in the field where soil and sediment may only be exposed to high concentrations of a given chemical for a limited period of time.

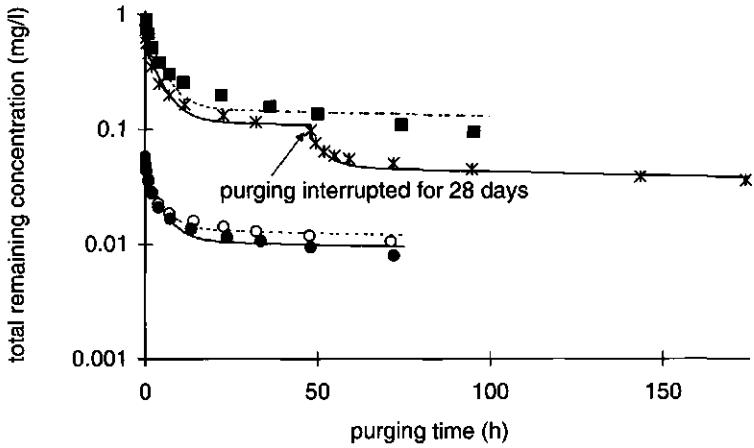

FIGURE 3.3. Fitted (solid lines) and predicted (dashed lines) curves obtained with the kinetic model. Measured data are represented by symbols; from Figure 3.1: high initial concentration ($\pm 1\,\mathrm{mg\,l^{-1}}$) measured directly after loading via the gas phase for 28 days (closed squares) and low initial concentrations ($\pm 0.1\,\mathrm{mg\,l^{-1}}$) measured after 28 (closed circles) and 70 (open circles) days total contact time, and from Figure 3.2: desorption with interrupted flow (stars).

Data Description

The kinetic model was fitted simultaneously to the experiment where desorption was followed in two subsequent steps (Figure 3.2) and to the continuous desorption curve of the soil suspension with a low initial QCB concentration that was measured after 28 days (Figure 3.1B closed circles). The validity of the fitted rate constants was tested by predicting the desorption curve with a high initial QCB concentration (Figure 3.1A closed squares) and the desorption curve with a low initial QCB concentration and a total contact time of 70 days (Figure 3.1B open circles) with the obtained parameters.

Figure 3.3 shows the fitted (solid lines) and predicted (dashed lines) desorption curves, the obtained parameters are given in Table 3.1. Although the desorption experiments differed in their experimental set-up; continuous, interrupted flow, and low or high initial QCB concentrations, the kinetic model gives a good description of all the data. The fitted desorption rate constants ($0.25\,\mathrm{h^{-1}}$ and $0.0016\,\mathrm{h^{-1}}$) are significantly smaller than the purge rate constant ($5.28\,\mathrm{h^{-1}}$) which implies that measured desorption

TABLE 3.1. Fitted Model Parameters[a]

$k_{a,l}^{app}$ (h^{-1})	0.40 ± 0.11
$k_{d,l}$ (h^{-1})	0.25 ± 0.03
$k_{a,f}^{app}$ ($(mg\,l^{-1})(mg\,l^{-1})^{-n}\,h^{-1}$)	0.00054 ± 0.00013
$k_{d,f}$ (h^{-1})	0.0016 ± 0.0001
n	0.78 ± 0.05
$C_{aq,t=0}{}^{b}$ ($mg\,l^{-1}$)	0.25 ± 0.04

[a] Parameters and standard deviations obtained from the simultaneous fit of the desorption experiment with interrupted flow and the desorption curve with a low initial QCB concentration that was measured after 28 days total contact time.

[b] Initial aqueous concentration for the desorption experiment with interrupted flow.

rates were not limited by purge rates. The predicted desorption for the soil suspension with a low initial concentration and a total contact time of 70 days follows the data relatively close. The calculated rate of desorption of the slow desorbing fraction is slightly slower than measured. However, the fit of the desorption experiment with interrupted flow is good.

Simulations

With the obtained parameters, the effect of different purging strategies on the removal of the slow desorbing fraction was simulated. Simulations were performed for the set-up as used in the experiments and for the following four purging strategies: (1) continuous purging, (2) intermittent purging with cycles of 48 hours of purging and 28 days of rest (1 cycle equals 30 days), (3) a 100-fold reduction of the purging rate constant after 30 days of purging, and (4) a reduction of the purging rate constant to a value equal to the slow desorption rate constant after 30 days of purging. The results of the simulations are given in Figure 3.4. Figure 3.4A shows the change of the bound QCB concentration in time and Figure 3.4B shows the change of the aqueous QCB concentration in time.

The simulations show that continuous purging with a large and constant purging rate coefficient is the fastest method to reduce both the bound and the aqueous QCB concentration. When the purging rate is 100-fold reduced after 30 days of purging, the aqueous QCB concentration increases significantly but removal of bound QCB is only slightly retarded. This indicates that the desorption rate constant is the rate-limiting factor for removal of slow desorbing QCB, for the system used in the experiments and for purging rate coefficients equal to or larger than $0.053\,h^{-1}$. Reduction

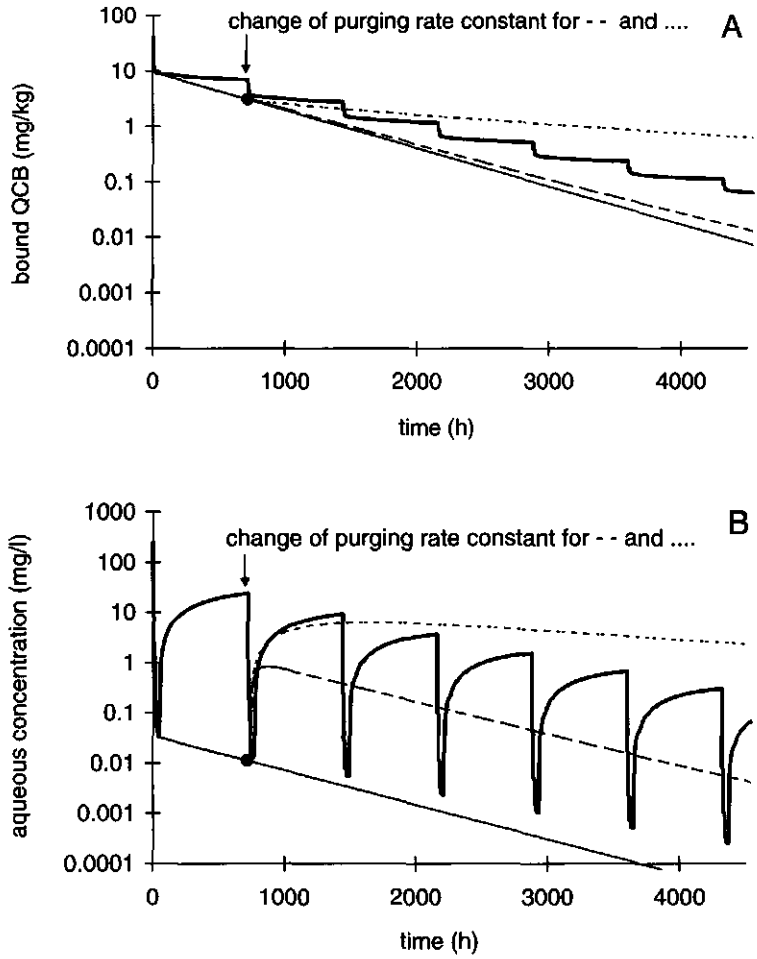

FIGURE 3.4. Simulated desorption of QCB from Wageningen Eng soil for different purging strategies; (1) continuous purging (——), (2) purging with interrupted flow (——), (3) 100-fold reduction of removal rate constant after 30 days (- - -), and (4) reduction of removal rate constant to value of slow desorption rate constant after 30 days (· · · ·). (A) Change of the bound concentration in time. (B) Change of the aqueous concentration in time.

of the purging rate coefficient after 30 days of purging to a value equal to the slow desorption rate coefficient, which is a 3422-fold reduction, shows a dramatically slower removal of bound QCB. For such a small purging rate coefficient, the purging has become rate-limiting. For intermittent purging, the total time needed to reach an equally low amount of bound QCB is longer than for continuous purging, but calculations showed that the total purging time is shorter. In the periods where no purging occurred, QCB redistributes from the slow and fast desorbing compartment to the aqueous phase. When the purging is stopped, the aqueous QCB concentration rises nearly 3 orders of magnitude in the simulated experiment. The non-linear sorption behaviour of QCB reduces the amount of bound QCB that can be removed in the 48 hours periods of purging (note that the y-axis is on a log scale, on a linear scale the reduction of the amount that could be removed in 48 hours is more dramatic).

Although the purging strategies used in these simulations may resemble remediation strategies used for polluted soils and sediments, the calculated times needed to reach a certain level cannot be extrapolated to field situations. However, the simulations may have implications for remediation of polluted soils or sediments. The simulations show that after removal of a fast desorbing fraction, efficient removal may be obtained at very slow purging or removal rates. However, the effect of slower removal rates on the aqueous concentration has to be taken into account. Although intermittent purging reduces the total purging time and may therefore be cost-effective, large fluctuations in the aqueous HOC concentration may be an unwanted side-effect.

ACKNOWLEDGEMENTS

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CHAPTER 4

Influence of Different Natural Organic Matter Fractions on the Desorption Kinetics of Pentachlorobenzene from Soil

Wendela Schlebaum, Gosse Schraa, Willem H. van Riemsdijk

ABSTRACT

Desorption kinetics of pentachlorobenzene from soluble humic acids, adsorbed humic acids and humin were compared to the desorption kinetics from soil. The humin fraction showed a higher affinity and similar release rates compared to the original soil. Both soluble and adsorbed humic acids showed a lower affinity and significantly faster release rates compared to humin and soil. Pentachlorobenzene could not be entrapped in the humic acid structure when humic acids were adsorbed to goethite after pentachlorobenzene had been adsorbed to the humic acids. The desorption kinetics of humin were shown to depend on the three-dimensional structure of the humin. HF/HCl treatment, which created a more expanded structure, resulted in a higher affinity for pentachlorobenzene with slightly faster release rates. Dried humin showed a significant reduction of the affinity for pentachlorobenzene. It was postulated that drying resulted in a more condensed structure with reduced possibilities for penetration of pentachlorobenzene into the humin structure. A kinetic model that could describe the sorption behaviour of pentachlorobenzene from Wageningen Eng soil was used to simulate the influence of the humin fraction on the sorption behaviour of the soil. The simulation and the measured desorption kinetics of the humin fraction indicated that humin is an important factor in the sorption behaviour of soils.

INTRODUCTION

Small release rates of hydrophobic organic compounds (HOCs) from soil and sediments with its concomitant problems for remediation have initiated a search for sorption mechanisms. Intraorganic matter diffusion has been mentioned as a possible sorption mechanism [9, 46, 62]. To investigate the influence of soil organic matter on the release rates of HOC from soil, different recognised organic matter classes can be studied.

Soil organic matter has been defined as the total of organic compounds in soil exclusive of undecayed plant and animal tissues, their "partial decomposition" products and the soil biomass [74]. The composition and nature of soil organic matter will depend on its origin and geological history. Natural organic matter has been operationally divided into fulvic acids, humic acids and humin. Fulvic acids are soluble in both acidic and alkali solutions, humic acids are only soluble in alkali solutions and humin is not soluble at all. Since these fractions have somewhat different chemical and physical characteristics, their affinity for HOC and the kinetics of their interactions may vary.

Different studies indicate that the affinity of organic matter for HOC is largely controlled by particle size and polarity [17, 27, 28]. With the decrease in their solubility the polarity of fulvic acids, humic acids, and humin decreases and their size and hydrophobicity increase. This corresponds with the observed order of the affinity for HOC: humin > humic acid > fulvic acid [17, 27, 28].

When intraorganic matter diffusion controls the observed slow release rates of HOCs from soils, the three-dimensional structure of humic substances should have an effect on the release rates. Expanded (soft or rubbery) and condensed (hard or glassy) organic matter fractions have been used to describe desorption kinetics of HOC from soil, see refs. in [46]. A more condensed and rigid structure is expected to restrict adsorption and desorption of HOC. Humin is assumed to have a more condensed structure and it is therefore expected that humin exhibits slower release rates than humic acids and fulvic acids. Adsorbed humic acids can also have a relatively rigid structure. Upon adsorption of humic acids to mineral surfaces, their three-dimensional structure may "collapse" and become more rigid and condense. Adsorption of a humic acid after the binding of a HOC may have an even larger effect since this could result in entrapment of the HOC. Since fulvic acids are relatively small, expanded, and hydrophilic, release of HOC from fulvic acids is assumed to be fast.

In this study, the desorption kinetics of pentachlorobenzene from soluble peat humic acids, adsorbed peat humic acids, humin and Wageningen Eng

soil are compared. The humin was extracted from Wageningen Eng soil. To test the relative importance of the humin fraction on the desorption kinetics of pentachlorobenzene from Wageningen Eng soil, a simulation was performed with a kinetic model that could describe the desorption kinetics of pentachlorobenzene from the soil [70].

MATERIALS AND METHODS

Materials

Purified peat humic acids (ppHA) were prepared from "Irish Peat" following the extraction procedure of the International Humic Substances Society, as modified by Reid et al. [63]. Based on proton titrations and their molecular weight, the radius of ppHA particles has been determined to be between 2 and 4 nm, depending on salt level [6]. The interactions between pentachlorobenzene and ppHA have been described in detail elsewhere [69]. Adsorbed humic acids were obtained via adsorption to goethite. Goethite was prepared following the method of Hiemstra et al. [38] and thereafter freeze-dried. The soil used in this study, Wageningen Eng soil, is a sandy soil which was air-dried and sieved. The organic carbon content of the sieve fraction used, < 0.5 mm, was 2.1%. The interactions between pentachlorobenzene and the sieve fraction < 0.5 mm are described elsewhere [70]. Humin was prepared by extracting the < 0.5 mm soil fraction three times with 0.1 M NaOH while a sand-fraction was discarded. The humin content of Wageningen Eng soil (<0.5 mm fraction) was 40% of the organic carbon content. After the alkali extraction, the humin suspension was dialysed for 2 weeks. Part of this batch was dried at 37 °C after the dialysis. The dried humin was ground with mortar and pestle. Another part of the humin suspension was extracted three times with 0.3 M HF : 0.1 M HCl. After extraction, the humin suspension was again dialysed for 2 weeks. The organic carbon content of the humin suspension was 4.2% before and 9.4% after HF/HCl extraction.

For all suspensions used in the experiments, the pH was set to 5 and 0.01 M $NaNO_3$ was added as background electrolyte. The ppHA solutions used in the experiments had a concentration of 0.5 g ppHA l^{-1}. Soil and humin suspensions had an organic carbon content of 0.25 g l^{-1} and 0.1 mM NaN_3 was added to prevent microbial growth.

Pentachlorobenzene (QCB, Merck, 98% pure) was used as hydrophobic organic pollutant. The loading of sorbent suspensions with QCB was done via the gas phase at 20 °C. Air was pumped through a glass tube filled with pure QCB. The air with QCB in the vapour state was led through the aqueous solution under continuous stirring. Gas flow in the adsorption

studies was approximately $70\,\mathrm{ml\,min^{-1}}$. The aqueous solubility of QCB was determined to be $0.30\,\mathrm{mg\,l^{-1}}$ with this method [69]. The adsorption period was 8 days for ppHA, and 28 days for humin and soil.

Goethite was added in-between the adsorption and the desorption period. After adsorption was stopped, the pH of the humic acid solution was set to pH 3 and goethite was added ($10\,\mathrm{g\,l^{-1}}$). This was done to enhance the adsorption of the humic acids to the goethite. After 4 hours, the pH of the solution, which was risen to 4.5, was manually raised to pH 5. The addition of goethite resulted in nearly complete ($> 99\%$) adsorption of the humic acids.

Analysis

To determine the QCB concentration, soil and humin suspensions were shaken for a minimum of 5 days with hexane while humic acid suspensions were extracted for at least 24 hours. The efficiency of the hexane extraction compared to a reflux extraction with hexane and acetone for the determination of the total initial QCB concentration in soil and humin suspensions was high: 95–105% [70]. The efficiency of the hexane extraction for the determination of the residual concentration in the desorption experiments is slightly lower [70]. QCB in the hexane phase was analysed with a Hewlett-Packard 5890 series II gas- chromatograph equipped with a HP 5 column and a Hewlett-Packard mass selective detector (series 5971) in selective ion monitoring mode.

Desorption Experiments

Desorption kinetics were measured in gas-purge experiments. Details of the experiments are described elsewhere [69]. Desorption experiments were done in triplicate since three identical suspensions (100 ml) were purged with nitrogen at the same time at 20 °C. QCB was trapped on Tenax columns. Hexane extracts of Tenax columns were concentrated, if necessary, under air after addition of an internal standard, 1,2,4,5-tetrachlorobenzene (Aldrich, 98% pure) in hexane. The total initial concentration for the desorption experiments was calculated by combining the amount recovered on the Tenax columns and the measured residual amount in the suspension. The recoveries for the soil and humin suspensions were 90–100%, the recoveries for the humic suspensions were 80–120%. A solution of QCB in water was purged to determine the rate with which the chemical was stripped from the water phase. The value obtained for the gas-purge rate constant (k_{gp}) was $5.28\,\mathrm{h^{-1}}$.

TABLE 4.1. QCB Concentration in Organic Matter and Soil Suspensions[a]

ppHA	$0.81 \pm 0.07\,\mathrm{mg\,l^{-1}}$
soil	$1.19 \pm 0.19\,\mathrm{mg\,l^{-1}}$
humin	$1.85 \pm 0.17\,\mathrm{mg\,l^{-1}}$
dried humin	$0.84 \pm 0.06\,\mathrm{mg\,l^{-1}}$
HF/HCl treated humin	$2.16 \pm 0.16\,\mathrm{mg\,l^{-1}}$

[a] The average total (sorbed + aqueous) QCB concentration is based on samples obtained after approximately 100 hours and until 28 days of loading via the gas phase.

RESULTS

As a result of the loading via the gas phase, the initial pentachlorobenzene (QCB) concentration at the start of the desorption experiments varied for the different sorbents according to their affinity for QCB. For all sorbents, the total (sorbed + aqueous) QCB concentration in the suspension reached a plateau after approximately 100 to 200 hours of loading and remained constant during an adsorption period of 28 days. Since the organic carbon concentrations were approximately equal for each suspension, the total QCB concentration in the suspensions may be taken as a measure of the relative affinity of the sorbent. The average QCB concentrations in the suspensions after reaching the plateau and until the end of the adsorption via the gas phase (28 days) are given in Table 4.1. The affinity for QCB of the humin extracted from Wageningen Eng soil was significantly higher than the affinity of ppHA and the affinity of the original soil (Table 4.1), as was expected. Both HF/HCl extraction and drying of humin affected the affinity of the humin.

Desorption kinetics of QCB from purified peat humic acids (ppHA), ppHA adsorbed on goethite, humin and soil are shown in Figure 4.1. Note that for all sorbents the organic carbon content was approximately equal and that this enables direct comparison of the desorption curves. The release rates of QCB from humin were considerably slower than release rates from both soluble and adsorbed ppHA. More than 10% of the initial amount of QCB in the humin suspension was very resistant to desorption. Although the initial QCB concentration in the humin suspension was higher than the initial QCB concentration in the suspension of the original soil, the desorption curves of humin and soil are remarkably similar (Figure 4.1).

The possible importance of bound humic acids on the overall desorption kinetics from soil was studied by adding a sorbent *after* QCB was bound to

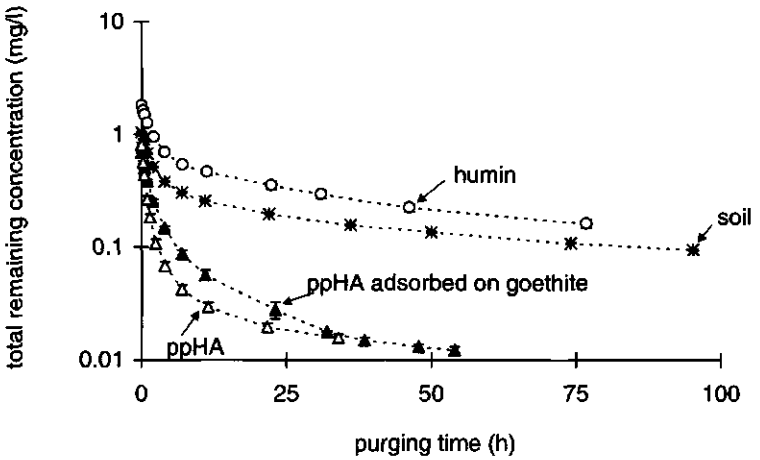

FIGURE 4.1. Desorption of QCB from soluble ppHA (open triangles), adsorbed ppHA (closed triangles), Wageningen Eng soil (stars) and humin (circles). Data of soluble ppHA and Wageningen Eng soil were taken from Schlebaum et al. [69] and [70], respectively. Error bars represent standard deviations but may be obscured by the symbol.

ppHA. The sorbent used was goethite, an iron oxide naturally present in soils, which could bind $> 99\%$ of all the humic acids present. Adsorption of ppHA to goethite after QCB was adsorbed to ppHA, resulted in a slightly slower release of QCB compared to desorption from soluble ppHA, as shown in Figure 4.1. QCB desorbed readily from both soluble and adsorbed ppHA; within 48 hours less than 2% of the initial QCB concentration remained.

Humin is almost by definition closely associated with inorganic soil constituents, as is illustrated by the organic carbon content of 4.2% for the humin derived from Wageningen Eng soil. To remove some of the mineral constituents from the humin fraction, the humin was treated with HF/HCl. After the HF/HCl extraction the organic carbon content of the humin was 9.4%. In Figure 4.2, desorption of QCB from the humin treated with HF/HCl is compared with desorption from the humin and soil from Figure 4.1. The HF/HCl extraction resulted in an increased relative affinity for QCB but also in a faster release rate. The initial QCB concentration was higher and the residual QCB concentration after 80 hours of purging was lower for HF/HCl treated humin than for the original humin suspension.

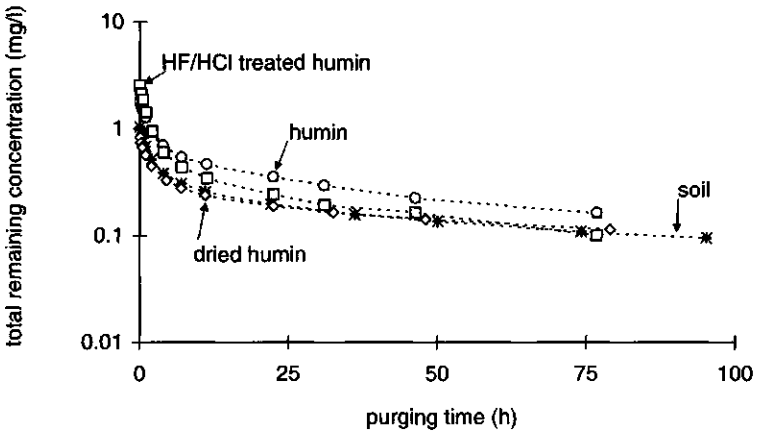

FIGURE 4.2. Desorption of QCB from HF/HCl treated humin (squares) and dried humin (diamonds). Desorption of QCB from humin (circles) and Wageningen Eng soil (stars) is given for comparison (data from Figure 4.1). Error bars represent standard deviations but may be obscured by the symbol.

Part of the original humin suspension was air-dried at 37 °C. This resulted in a dramatic reduction of the affinity for QCB, as shown in Table 4.1. After drying, the humin seemed to resist resuspension. During the loading via the gas phase, the QCB concentration reached a plateau within 200 hours and remained constant. This suggests that the structure of the dried humin did not change during 28 days of adsorption via the gas phase. The release rates of QCB from dried humin were somewhat slower than the release rates from soil; the initial QCB concentration was lower but the residual QCB concentration was higher compared to Wageningen Eng soil, as can be seen in Figure 4.2.

DISCUSSION

The different organic matter fractions that were investigated in this study showed different affinities for QCB. The affinity of humin for QCB was significantly larger than the affinity of ppHA for QCB. This was expected since humin is assumed to be more hydrophobic than humic acids. The affinity for QCB of humin was also larger than the affinity for QCB of the soil. The organic carbon of the soil consisted of 40% humin with a high affinity for QCB and 60% in alkali soluble organic matter such as

humic acids and fulvic acids with a low affinity for QCB. A rough calculation based on ppHA and humin behaviour, would indicate that the expected sorbed + aqueous QCB concentration in the soil suspension would be $0.6 \times 0.81\,\mathrm{mg\,l^{-1}} + 0.4 \times 1.85\,\mathrm{mg\,l^{-1}} = 1.23\,\mathrm{mg\,l^{-1}}$. This is not significantly different from the measured QCB concentration in the soil suspension ($1.19\,\mathrm{mg\,l^{-1}}$).

Dried humin had an affinity for QCB which was more or less equal to the affinity of ppHA. Drying is not expected to alter the humin composition and it is certainly not expected that humin will become hydrophilic after drying. The relatively low affinity of dried humin for QCB therefore seems to indicate that the available "sites" for QCB adsorption were reduced as a result of the drying. We postulate that the reduction of sites was caused by a condensation of the humin structure. The condensed structure reduced the amount of QCB that could penetrate into the humin structure. The higher affinity of HF/HCl treated humin for QCB may have resulted from an increased availability of hydrophobic sites caused by a more expanded structure. HF/HCl treatment can remove minerals or metals that form "bridges" within the humin structure or between different humin particles thereby creating a more expanded structure.

An increase in affinity for QCB of HF/HCl treated humin resulted in faster desorption while a decreased affinity for QCB of dried humin resulted in slower desorption. For HF/HCl treated humin, the expanded structure can cause desorption to be less restricted explaining the observed increase in release rates. Similarly, a more condensed structure as a result of drying may cause desorption to be more restricted and slower. Swelling of the organic matter matrix was postulated by Brusseau et al. [13] to explain the observed increase in desorption rates with increasing co-solvent concentration. Several studies indicate that extraction with HF/HCl may not only result in a loss of inorganics but also of organic carbon, see refs. in [64]. The removal of relatively soluble organic matter residues might result in an increased relative affinity but it is not able to explain the observed increase in release rates. In accord with the postulated condensation of the humin structure, drying of (bio)polymers has been reported to result in a change from a rubbery to a glassy state, see e.g. [1, 24]. This change in state changes the polymer structure from expanded and flexible to condensed and rigid. A more condensed or glassy humin structure is in agreement with the slow release rates of dried humin. When dried polymers are reswelled the transition from the glassy state to the rubbery state may occur relatively slowly in poor solvents [24]. Since water is probably a rather poor solvent for humin, it may not be able to break the physical cross-linkages present in

the glassy state. The latter could explain the seemingly irreversible change of the humin structure.

The adsorption of ppHA to goethite after QCB had been adsorbed to ppHA resulted in slower desorption but did not result in a visible entrapment of QCB. The change of the three-dimensional structure of ppHA upon adsorption to goethite could have resulted in a more condensed and rigid ppHA with concomitant slower release rates. Garbarini and Lion [26] and Schlautman and Morgan [68] demonstrated that upon adsorption the affinity of humic or fulvic acids for HOC decreases. Similar to the changes in affinity and desorption rates of the humin fractions, slower release rates of adsorbed ppHA could be correlated with a lower affinity. Compared to humin, the influence of the three-dimensional structure of ppHA on the desorption behaviour of QCB is small, but this is caused by the smaller size of ppHA.

It has been suggested in the literature that the humin fraction consists of humic acids strongly bound to inorganic soil constituents. However, spectroscopic evidence has indicated that the humin fraction of a soil differs significantly from the humic acid fraction of the same soil [33]. The measured desorption kinetics of adsorbed ppHA and humin also indicate that bound humic acids are not the same as humin. Rice and MacCarthy [64, 66] subdivided humin into four separate fractions by extraction with an organic solvent: (1) solvent extractable lipid referred to as bitumen, (2) unextractable or bound lipid, (3) a fraction resembling humic acid referred to as bound humic acid, and (4) a mineral component referred to as insoluble residue. The bound humic acid fraction conforms to the operational definition of humic acid but it is only released after disaggregation of the humin [66]. Rice and MacCarthy [66] have proposed that the humin can be viewed as an aggregation of bitumen, bound humic acids, bound lipids and an inorganic fraction. Such a matrix can show a high affinity for HOC while desorption kinetics are influenced by the structure of the organic matter matrix.

Sorption kinetics of HOC from soils and sediments have been described in the literature using rubbery or expanded and glassy or condensed organic matter fractions, see refs. in [46]. The expanded fraction shows fast desorption kinetics and the condensed fraction shows slow desorption kinetics. This corresponds with the influence of the three-dimensional structure of ppHA and humin on the desorption kinetics of QCB. The question is now, whether the sorption behaviour of the organic matter fractions can

control the sorption behaviour of the soil. Based on the measured similarities between the desorption curve of the humin and of the soil, the humin can be responsible for the desorption behaviour of the soil.

The presence of more physically condensed and chemically reduced organic matter in soils has been shown to result in an increased affinity for HOC and an increased non-linear sorption behaviour [39]. Non-linear sorption behaviour is a direct consequence of the presence of a limited number of sites with a high energy for sorption. These sites could occur when sorbate molecules interact at multiple points with the sorbent, when there is steric hindrance to desorption or adsorption, or when a sorbate induces a change in the sorbent [62]. Chiou and Kile [16] demonstrated for a peat soil and a mineral soil that at low HOC concentrations, sorption isotherms were non-linear while at high HOC concentrations, sorption isotherms became linear. They attributed the linear part of the sorption isotherm to a partitioning process. Sites with a high sorption energy were postulated to result from adsorption of HOC to charcoal-like substances [16]. Non-linear sorption behaviour has also been reported for soluble humic acids [69] and adsorbed humic acids, see e.g. [53]. However, given the similarities in desorption behaviour of QCB from humin and from soil and the reported correlation between non-linear sorption behaviour and soil samples with more physically condensed and chemically reduced soil organic matter, we expect that these sites will be predominantly present in the humin fraction.

Simulation

Ideally, the relative importance of the different organic matter fractions for the desorption kinetics of a soil is tested by predicting the desorption kinetics of a soil. To be able to predict the desorption kinetics of a soil, the kinetics of the different organic matter fractions have to be described and related to their relative abundance in the soil. For the different organic matter fractions used in this study, only a kinetic model describing desorption kinetics from ppHA is available [69]. Previous studies with ppHA and with Wageningen Eng soil indicated that, to obtain a model able to predict other experiments, a relatively large data-set obtained with different experimental set-ups is needed [69, 70]. This implies that although a description of the humin data may be found, its predictive capability will be limited. Therefore, we used the kinetic model of Wageningen Eng soil to simulate the desorption behaviour of the humin based on a description of the desorption behaviour of the soil.

The kinetics of the interactions between QCB and Wageningen Eng soil were described with a model that consists of a fast desorbing fraction with

a linear sorption isotherm and first-order kinetics, and a slow desorbing fraction with a Freundlich isotherm and n^{th}-order kinetics [70]. The slow desorbing fraction represents sorption to high affinity sites while the fast desorbing fraction represents a partitioning process. Diffusion processes may play a role in the model since kinetic models based on first-order or non-linear rate coefficients have been shown to be able to give in some cases an equally good description of measured sorption kinetics compared to diffusion models [50, 59, 82].

In the simulation, we assume that the sorption behaviour of humin is solely responsible for the sorption behaviour of Wageningen Eng soil. The humin represents 40% of the total organic carbon of the soil, indicating that 60% of the organic carbon content consists of potentially soluble organic matter fractions such as fulvic and humic acids. We assume that this potentially soluble fraction shows a lower affinity and release rates equal to or faster than ppHA, and that it therefore has a negligible effect on the desorption kinetics of the soil.

The equations describing the kinetics of the interactions are given in Table 4.2. The differential equations were solved numerically. The values of the parameters given in Table 4.2 resulted from a simultaneous fit of two different experiments in which QCB was desorbed from Wageningen Eng soil [70]. For the desorption of QCB from soil and humin (data from Figure 4.1), the amount of QCB bound to the different fractions at the start of the desorption experiment was calculated using the measured total initial QCB concentration and the assumption that, at the start of the desorption experiment, equilibrium had been reached. The latter assumption was made since the adsorption via the gas phase and previous studies with Wageningen Eng soil [70] suggested that equilibrium was reached within the adsorption period.

The adsorption rate constants for Wageningen Eng soil given in Table 4.2, are linear with the sorbent concentration and they are therefore apparent adsorption rates. To obtain the true adsorption rate constants (k_{a}), the apparent adsorption rate constants ($k_{\text{a}}^{\text{app}}$) can be normalised to the sorbent concentration. When the assumption is made that humin is responsible for the observed sorption behaviour from soil, the apparent adsorption rate constants of the soil have to be normalised to the humin content. The apparent adsorption rate constants for the humin suspension ($k_{\text{a}}^{\text{app,h}}$) were determined as follows:

$$k_{\text{a}}^{\text{app,h}} = \frac{k_{\text{a}}^{\text{app}}}{f_{\text{h}} f_{\text{oc}}^{\text{s}} S^{\text{s}}} f_{\text{oc}}^{\text{h}} S^{\text{h}}, \tag{4.1}$$

TABLE 4.2. Kinetic Model for Wageningen Eng Soil [70]

Equations[a]

$$\frac{dq_{\mathrm{l}}S}{dt} = -k_{\mathrm{d,l}}q_{\mathrm{l}}S + k_{\mathrm{a,l}}^{\mathrm{app}}C_{\mathrm{aq}}$$

$$\frac{dq_{\mathrm{f}}S}{dt} = -k_{\mathrm{d,f}}q_{\mathrm{f}}S + k_{\mathrm{a,f}}^{\mathrm{app}}C_{\mathrm{aq}}^{n}$$

$$\frac{dC_{\mathrm{aq}}}{dt} = k_{\mathrm{d,f}}q_{\mathrm{f}}S + k_{\mathrm{d,l}}q_{\mathrm{l}}S - k_{\mathrm{a,f}}^{\mathrm{app}}C_{\mathrm{aq}}^{n} - k_{\mathrm{a,l}}^{\mathrm{app}}C_{\mathrm{aq}} - k_{\mathrm{gp}}C_{\mathrm{aq}}$$

Parameters[a]

$k_{\mathrm{d,l}}$ (h^{-1})	0.25
$k_{\mathrm{a,l}}^{\mathrm{app}}$ (h^{-1})	0.40
$k_{\mathrm{d,f}}$ (h^{-1})	0.0016
$k_{\mathrm{a,f}}^{\mathrm{app}}$ $((\mathrm{mg\,l}^{-1})(\mathrm{mg\,l}^{-1})^{-n}\,\mathrm{h}^{-1})$	0.00054
n	0.78

[a] q_{l} and q_{l} ($\mathrm{mg\,kg}^{-1}$) are the amount of pollutant bound to the linear and Freundlich site respectively; S ($\mathrm{kg\,l}^{-1}$) is the sorbent concentration; C_{aq} ($\mathrm{mg\,l}^{-1}$) is the aqueous concentration; n is the Freundlich exponent which is a measure of the heterogeneity; $k_{\mathrm{d,f}}$ (h^{-1}) and $k_{\mathrm{a,f}}^{\mathrm{app}}$ $((\mathrm{mg\,l}^{-1})(\mathrm{mg\,l}^{-1})^{-n}\,\mathrm{h}^{-1})$ are the desorption and apparent adsorption rate constant of the Freundlich site; $k_{\mathrm{d,l}}$ (h^{-1}) and $k_{\mathrm{a,l}}^{\mathrm{app}}$ (h^{-1}) are the desorption and apparent adsorption rate constant of the linear site and k_{gp} (h^{-1}) is the gas-purge rate constant.

where $S^{\mathrm{s,h}}$ ($\mathrm{kg\,l}^{-1}$) is the sorbent concentration of the soil or humin suspension, $f_{\mathrm{oc}}^{\mathrm{s,h}}$ $((\mathrm{g\,OC})(\mathrm{g\,sorbent})^{-1})$ is the organic carbon (OC) fraction of the soil or humin, and f_{h} $((\mathrm{g\,OC\,humin})(\mathrm{g\,OC\,soil})^{-1})$ is the humin fraction of the soil organic carbon. This resulted in a $k_{\mathrm{a,l}}^{\mathrm{app,h}}$ of $1.0\,\mathrm{h}^{-1}$ and a $k_{\mathrm{a,f}}^{\mathrm{app,h}}$ of $0.0014\,\mathrm{h}^{-1}$. The values of the desorption rate constants and the Freundlich parameter n for humin are assumed to be equal to the values for soil (given in Table 4.2). The simulated desorption of QCB from humin and the description of the desorption of QCB from soil are given in Figure 4.3. The simulated desorption of QCB from humin follows the data reasonably close for 25 hours, although we excluded interactions of QCB with other organic matter fractions and neglected the soil particle structure. After 25 hours, the simulated desorption rate is significantly slower than the measured desorption rate (Figure 4.3). The description of the desorption of QCB from soil also overestimates the slow desorption rate but less than for humin.

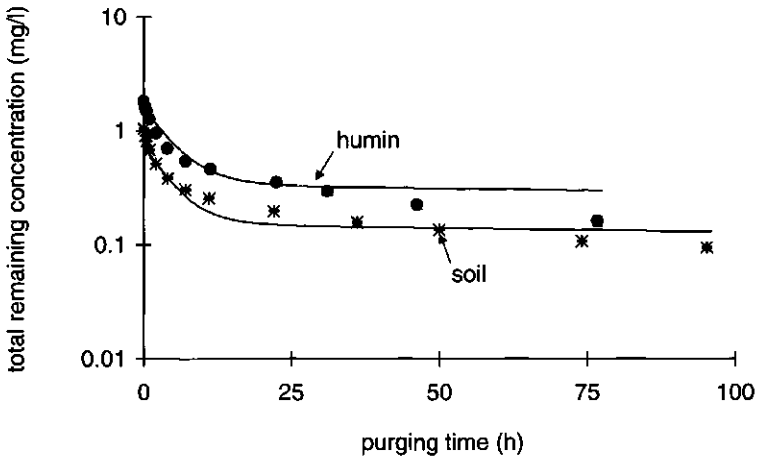

FIGURE 4.3. Predicted desorption curves (solid lines) obtained with the kinetic model for Wageningen Eng soil (stars) and humin extracted from this soil (circles). Measured data are represented by symbols and dashed lines.

The measured desorption kinetics of the humin fraction and the simulated desorption of QCB from humin indicate that humin may be a key-factor in the sorption behaviour of soils.

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CHAPTER 5

Desorption Kinetics and Microbial Degradation Kinetics of 2,5-Dichlorobiphenyl in Soil

Wendela Schlebaum, Esther Driessen, Aleksandra Badora, Willem H. van Riemsdijk and Gosse Schraa

ABSTRACT

The rate at which organic pollutants are degraded in contaminated soils depends on the intrinsic activity of the bacteria and the sorption and desorption kinetics of the contaminant. It is assumed that degradation rates in soil can be predicted when the activity of the degrading organisms and the sorption and desorption kinetics are known. We predicted degradation of 2,5-dichlorobiphenyl (2,5-PCB) sorbed to different sieve fractions of a soil by *Pseudomonas* sp. strain JHK. The prediction was based on measured desorption kinetics of 2,5-PCB from these different sieve fractions and measured degradation kinetics in the absence of soil. Measured desorption kinetics were very similar for the three sieve fractions and were described with a model that incorporated non-linear sorption behaviour. Measured degradation kinetics in batches without soil could be described when inactivation of the bacteria was taken into account. The sorption-degradation model showed that the initial desorption rates of the majority of the bound 2,5-PCB were not rate-limiting for the degradation. Desorption of the slow desorbing 2,5-PCB fraction was rate-limiting for the degradation. The predicted degradation rates of 2,5-PCB in the different soil suspensions were slower than measured degradation rates. This may have resulted from a higher activity and/or lower inactivation of the bacteria in the batches with soil compared to the batches without soil. This implies that laboratory measurements of degradation with (isolated) bacterial strains in the absence of soil may not give an accurate estimate of the microbial activity in the field.

INTRODUCTION

Microbial degradation of hydrophobic organic contaminants (HOCs) such as polychlorinated biphenyls (PCBs) in soils is strongly influenced by the interactions of the contaminant with the soil, see e.g. [3]. In most studies, the binding of HOC to soil renders the HOC unavailable for microbial degradation [77]. Sorption and desorption kinetics can therefore have a large influence on the microbial degradation of HOCs in soil. It is assumed that degradation rates in soil can be predicted when both the activity of the degrading organisms and the desorption kinetics are known.

Desorption kinetics limit the rate of degradation in soil when the intrinsic rate of degradation is faster than the rate of desorption. When the rate of degradation is slower than the desorption rate, desorption kinetics will not be rate-limiting for the degradation in soil. However, in that case, equilibrium sorption can still influence the degradation since sorption reduces the contaminant concentration in the aqueous phase. Part of the HOC is therefore shielded from the micro-organisms, assuming that sorbed HOC is unavailable. In recent studies, the non-linear nature of the interactions between HOC and soil were demonstrated, see e.g. [29, 40, 85]. Non-linear sorption results in slower desorption than adsorption, especially the last stages of desorption are extremely slow [20]. These slower release rates are expected to hamper microbial degradation of organic contaminants in soil.

In this study, desorption kinetics of 2,5-dichlorobiphenyl (2,5-PCB) were measured and modelled for different sieve fractions of Wageningen Eng soil. In previous studies, measured desorption kinetics of pentachlorobenzene and Wageningen Eng soil could be described with a model that incorporated non-linear sorption [70]. Degradation kinetics of 2,5-PCB by *Pseudomonas* sp. strain JHK [35] were measured and modelled in the absence of soil. In the sorption-degradation model, the model describing sorption and desorption kinetics and the model describing the degradation kinetics were coupled. The degradation of 2,5-PCB in the presence of the different sieve fractions of Wageningen Eng soil was predicted with the sorption-degradation model and with the obtained degradation, sorption and desorption rate constants of the individual experiments. The predictions were compared to measured degradation rates.

MATERIALS AND METHODS

Materials and Solution Preparation

The soil used, Wageningen Eng soil, is a sandy soil which was air-dried and sieved. The sieve fractions used in this study were < 0.063 mm, 0.125–0.25 mm, and < 0.5 mm. Their organic carbon (OC)-content was 5.8, 1.4 and 2.0%, and their humin content was 45, 29 and 40% of the total OC, respectively. The sieve fraction < 0.5 mm contained 40% of the fraction 0.25–0.5 mm, 30% of the fraction 0.125–0.25 mm, 14% of the fraction 0.063–0.125 mm, and 16% of the fraction < 0.063 mm. All soil suspensions in the experiments had an OC-content of $0.25\,g\,l^{-1}$. All suspensions and solutions were in mineral medium (pH 7.3) that contained per liter of demineralised water: 7 g $Na_2HPO_4{\cdot}2H_2O$; 2 g KH_2PO_4; 1 g $(NH_4)_2SO_4$; 0.01 g Fe(III)NH_4citrate; 0.2 g $MgSO_4{\cdot}7H_2O$; 1 mg $Ca(NO_3)_2{\cdot}4H_2O$ and 1 ml of a trace element solution (containing per liter: 100 mg $ZnSO_4{\cdot}7H_2O$; 30 mg $MnSO_4$; 300 mg H_3BO_3; 200 mg $CoSO_4$; 20 mg $NiSO_4$; 10 mg $CuSO_4{\cdot}5H_2O$; 30 mg $Na_2MoO_4{\cdot}2H_2O$).

The loading of mineral medium with 2,5-dichlorobiphenyl (2,5-PCB, C.N. Schmidt B.V., Amsterdam, The Netherlands) was done via the gas phase at 20 °C. Air was pumped at approximately $70\,ml\,min^{-1}$ through a glass tube filled with Tenax and pure 2,5-PCB. The air with 2,5-PCB in the vapour state was led through the medium under continuous stirring for a period of 4–6 days. This medium with 2,5-PCB was used either directly or a known volume was added to a concentrated soil suspension (in mineral medium; pH was checked prior to addition of 2,5-PCB solution; final OC-concentration was $0.25\,g\,l^{-1}$). After an adsorption period of 14 days at 4 °C (suspensions were stirred), either a desorption experiment or a degradation experiment was started.

Analysis

To determine the 2,5-PCB concentration, soil suspensions were shaken for a minimum of 5 days with hexane while aqueous solutions were extracted for at least 24 hours. Comparison with a reflux method indicated that for the determination of total initial concentrations, the used method provided good extraction efficiencies (95–105%, [70]). The efficiency of the hexane extraction for determination of residual concentrations was somewhat lower but still good [70]. This may have resulted in an underestimation of the slow desorbing fraction. 2,5-PCB in the hexane phase was analysed with a Hewlett-Packard 5890 series II gas-chromatograph equipped with a HP 5 column and a Hewlett-Packard mass selective detector (series 5971) in selective ion monitoring mode.

Desorption Kinetics

Desorption kinetics were followed in gas-purge experiments. Desorption experiments, of which details are described elsewhere [69], were done in triplicate since three identical soil suspensions (100 ml) were purged simultaneously with nitrogen at 20 °C. 2,5-PCB was trapped on Tenax columns. Hexane extracts of these Tenax columns were concentrated, if necessary, under air after addition of the internal standard, 1,2,4,5-tetrachlorobenzene (Aldrich, 98% pure) in hexane. At the end of a desorption experiment, at least 80 ml of the soil suspension was transferred to 4–5 extraction tubes. The initial total 2,5-PCB concentration for the desorption experiments was calculated by combining the amount recovered on the Tenax columns and the residual amount in the suspension. The recoveries (ratio between the calculated and the measured initial 2,5-PCB concentration) were 90–110%. A solution of 2,5-PCB in medium was purged to determine the rate with which the chemical is stripped from the water phase. The value obtained for the gas-purge rate constant (k_{gp}) was 5.06 h^{-1}.

Degradation Kinetics

2,5-PCB is transformed by *Pseudomonas* sp. strain JHK into 2,5-dichlorobenzoate [35]. The cells were pregrown on biphenyl crystals and were incubated at 30 °C for 48 hours. After 48 hours, remaining crystals were removed by sieving the cell-suspension over a metal sieve. The cells were washed twice, counted and diluted until 10^9 cells ml^{-1}. The cell suspension was stored overnight at 4 °C, and 1 hour before inoculation the cell suspension was placed at 20 °C. Cells were counted again after the inoculation.

For the degradation experiments, 20-ml samples of a 2,5-PCB soil suspension or 20-ml samples of an aqueous 2,5-PCB solution were transferred to 25-ml tubes the day before the inoculation. Tubes were closed with Viton stoppers. Since the activity of different cell suspensions may vary, degradation experiments in the presence and absence of a sieve fraction of the soil started simultaneously using the same cell suspension. In this way, an individual microbial activity was obtained for each degradation experiment in the presence of a sieve fraction. Tubes were inoculated with 0.1 ml of the cell suspension, resulting in a final cell concentration of $\pm 5 \times 10^6$ cells ml^{-1}. For each time sample, degradation in 3 tubes was stopped by adding 2 ml of 10 M HCl to the suspensions. Controls without strain JHK were present to ensure that the loss of 2,5-PCB could be ascribed to degradation by strain JHK.

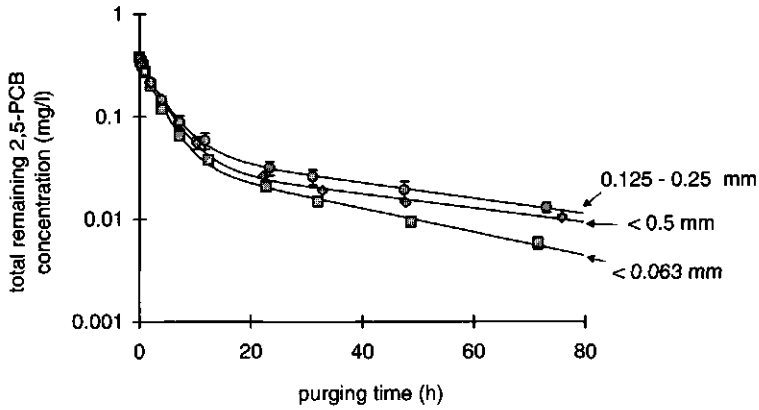

FIGURE 5.1. Desorption of 2,5-PCB from different sieve fractions of Wageningen Eng soil. Measured data are represented by symbols, solid lines are obtained with the sorption model (eqs. 5.1, 5.2, and 5.3). Fractions used are $<$ 0.5 mm (diamonds), 0.125–0.25 mm (circles), and $<$ 0.063 mm (squares). Error bars represent standard deviations but may be obscured by the symbol.

RESULTS AND DISCUSSION

Experimental Results Desorption Kinetics

The measured desorption kinetics of 2,5-PCB from three sieve fractions of Wageningen Eng soil is shown in Figure 5.1. Desorption of 2,5-PCB from the soil fractions was relatively fast. Within 24 hours more than 90% of the total initial 2,5-PCB concentration was removed. After 70 hours of purging only 1.5–4% of the total initial 2,5-PCB concentration remained.

The sieve fractions differed in aggregate size, composition, and also in humin content. Humin is the insoluble organic matter fraction in soil and is believed to be larger, more hydrophobic, and to have a more condensed structure than the potentially soluble organic matter fraction which contains fulvic acids and humic acids. Since all soil suspensions had the same organic carbon content, the desorption behaviour of the fractions may be compared in Figure 5.1. The desorption curves of the three fractions are remarkably similar in the first 24 hours of the desorption experiment. Differences between the desorption curves of the fractions $<$ 0.5 mm and 0.125–0.25 mm in the tail of the desorption curves are also small. However, the fraction $<$ 0.063 mm does show a significantly faster desorption rate for the slow desorbing fraction. It was expected that this sieve fraction,

which had a higher humin content compared to the other two sieve fractions, would show slower desorption rates. We demonstrated in previous studies with Wageningen Eng soil ($< 0.5\,\mathrm{mm}$), that the desorption rates of pentachlorobenzene from humin are in the same range as the desorption rates from soil [71]. Therefore, although an increase of the humin content is correlated with a slightly faster desorption for the three sieve fractions, one cannot conclude that humin does not influence the desorption behaviour of the sieve fractions.

Since the differences between the desorption curves of the three sieve fractions are relatively small and since there is no direct correlation between aggregate size, aggregate composition or humin content, the data do not seem to point to the presence of a dominant sorption mechanism. Chiou and Kile [16] and Pignatello and Xing [62] suggested that a limited number of sites exists that exhibit high energies for sorption. These sites account for non-linear sorption of organic contaminants to soil. Chiou and Kile [16] demonstrated that at low HOC concentrations sorption isotherms were non-linear and that at high HOC concentrations sorption isotherms became linear. They suggested that sites with high energies of sorption are present in natural charcoal-like substances. An equal amount of charcoal-like substances in the two larger sieve fractions and a smaller amount in the sieve fraction $< 0.063\,\mathrm{mm}$ could explain the observed desorption behaviour. Chiou and Kile attributed the linear part of the sorption isotherm to a partitioning process. Since partitioning is a rather non-specific process with fast kinetics, the initial desorption behaviour for the three sieve fractions can be very similar, especially since the organic carbon contents are equal.

Modelling Desorption Kinetics

Several features of sorption of HOC on soil suggest that a limited number of sites exists that exhibit high energies for sorption [16, 62]. These sites were described in the used sorption model by a compartment with a Freundlich sorption isotherm and corresponding n^{th}-order kinetics. Partitioning was described by a separate second compartment characterised by a linear sorption isotherm and first-order kinetics. The equations used to

describe the kinetics of the interactions are [70]:

$$\frac{dq_{\mathrm{f}}S}{dt} = -k_{\mathrm{d,f}}q_{\mathrm{f}}S + k_{\mathrm{a,f}}^{\mathrm{app}}C_{\mathrm{aq}}^{n}, \tag{5.1}$$

$$\frac{dq_{\mathrm{l}}S}{dt} = -k_{\mathrm{d,l}}q_{\mathrm{l}}S + k_{\mathrm{a,l}}^{\mathrm{app}}C_{\mathrm{aq}}, \tag{5.2}$$

$$\frac{dC_{\mathrm{aq}}}{dt} = k_{\mathrm{d,f}}q_{\mathrm{f}}S + k_{\mathrm{d,l}}q_{\mathrm{l}}S - k_{\mathrm{a,f}}^{\mathrm{app}}C_{\mathrm{aq}}^{n} - k_{\mathrm{a,l}}^{\mathrm{app}}C_{\mathrm{aq}} - k_{\mathrm{gp}}C_{\mathrm{aq}}, \tag{5.3}$$

where q_{l} and q_{f} ($\mathrm{mg\,kg^{-1}}$) are the amount of pollutant bound to the linear and Freundlich compartment, respectively; C_{aq} ($\mathrm{mg\,l^{-1}}$) is the aqueous concentration; S ($\mathrm{kg\,l^{-1}}$) is the sorbent concentration; $k_{\mathrm{d,f}}$ ($\mathrm{h^{-1}}$) and $k_{\mathrm{a,f}}^{\mathrm{app}}$ ($(\mathrm{mg\,l^{-1}})(\mathrm{mg\,l^{-1}})^{-n}\,\mathrm{h^{-1}}$) are the desorption and apparent adsorption rate constant of the Freundlich compartment; n is the Freundlich exponent which is a measure of the heterogeneity; $k_{\mathrm{d,l}}$ ($\mathrm{h^{-1}}$) and $k_{\mathrm{a,l}}^{\mathrm{app}}$ ($\mathrm{h^{-1}}$) are the desorption and apparent adsorption rate constants of the linear compartment and k_{gp} ($\mathrm{h^{-1}}$) is the gas-purge rate constant. The sorption isotherms of the Freundlich and linear compartment can be found since at equilibrium $dqS/dt = 0$, and solving equations 5.1 and 5.2 shows that the overall binding coefficients are a function of the rate coefficients. In the above equations, the adsorption rate constants are linear with the sorbent concentration and they are therefore apparent adsorption rates. To obtain the normalised adsorption rate constant (k_{a}) the apparent adsorption rate can be divided by the sorbent concentration.

The amount of 2,5-PCB bound to the two compartments at the start of a desorption experiment can be calculated using equations 5.1, 5.2, and 5.3 (with $k_{\mathrm{gp}} = 0$). However, since adsorption and desorption occurred at different temperatures, the rate coefficients will be different for the adsorption and desorption period according to the Arrhenius equation, see e.g. [72]. To be able to calculate the change of the adsorption and desorption rate constants with a change of temperature, values for the activation energies (E_{act}) are needed. Activation energies for non-ionic HOC appear to be relatively independent of compound and sediment [19, 78]. Therefore, we used the average activation energy for fast desorption of non-ionic HOC from soils and sediments given by Ten Hulscher and Cornelissen [78] ($E_{\mathrm{d,l}}^{\mathrm{act}} = 26 \pm 14\,\mathrm{kJ\,mol^{-1}}$). The latter study showed that, for the fraction with fast sorption kinetics, the average activation energy for adsorption is not significantly different from the average activation energy for desorption. Therefore, we used the same value for both activation energies ($E_{\mathrm{d,l}}^{\mathrm{act}} = E_{\mathrm{a,l}}^{\mathrm{act}} = 26\,\mathrm{kJ\,mol^{-1}}$). Identical adsorption and desorption activation energies indicate that sorption does not result in an energy gain

through sorbent-sorbate interactions. Since sorption does occur, this suggests that sorption, and in this case partitioning, is an entropy-driven process. For the slow adsorbing and desorbing fraction we used the average activation energies for slow sorption and desorption of different PCBs, chlorinated benzenes in lab-contaminated sediments given by Cornelissen et al. [19] ($E_{a,f}^{act} = 59 \pm 7\,kJ\,mol^{-1}$ and $E_{d,f}^{act} = 67 \pm 4\,kJ\,mol^{-1}$). The values of the activation energies are given in Table 5.1 together with other parameters that were used in the modelling. Cornelissen et al. [19] suggested that the measured activation energies indicated that the slow desorbing compartment consisted of remote organic regions and not of narrow water-saturated pores. It should be noted that the above activation energies were calculated for rate constants from a two-compartment model with two linear (first-order kinetics) fractions in series.

To describe the desorption kinetics, 5 parameters (4 rate constants and n) needed to be fitted to the data. However, the desorption curves of 2,5-PCB from the fractions did not contain sufficient "information" for an accurate estimate of n. In studies with pentachlorobenzene and the fraction $< 0.5\,mm$ from Wageningen Eng soil, n was determined to be equal to 0.78 ± 0.05 [70]. This value was determined using a data-set which contained more information than the desorption curves of 2,5-PCB from the different sieve fractions. Since n is a measure for the heterogeneity of the soil, we felt it was appropriate to use the same value of n for 2,5-PCB as for pentachlorobenzene. 2,5-PCB and pentachlorobenzene are very similar in hydrophobicity and it is not unlikely that they experience the same heterogeneity. Furthermore, in the literature n seems to be fairly constant within the range 0.6–0.9 [29, 40, 85]. With n equal to 0.78 for all sieve fractions, we further assumed that the subfractions $< 0.063\,mm$ and 0.125–0.25 mm had similar heterogeneities as the fraction $< 0.5\,mm$.

Starting from an initial guess, the four rate constants were fitted to the experimental data using a least-squares criterion and a Newton-Raphson method. Each iteration step involved numeric integration of the set differential equations. We used a standard fourth order Runge-Kutta method for this purpose.

Figure 5.1 shows the fitted desorption curves for the three soil fractions. The fitted rate constants and the parameters used are given in Table 5.1. The used sorption model gives a good description of the data. Therefore, the assumptions made (n equal to 0.78 and activation energies from literature) seem reasonable. The standard deviations of the fitted parameters show that the differences between the fractions 0.125–0.25 mm and $< 0.5\,mm$ are not significant. Only the desorption rate constant of the

TABLE 5.1. Parameters Used in Sorption-Degradation Model

	sieve fraction < 0.5 mm (experiment A)	sieve fraction 0.125–0.25 mm (experiment B)	sieve fraction < 0.063 mm (experiment C)
$k_{a,l}^{app}$ $(h^{-1})^a$	3.8 ± 3.1	2.0 ± 0.8	2.2 ± 1.1
$k_{d,l}$ $(h^{-1})^a$	0.45 ± 0.18	0.34 ± 0.05	0.44 ± 0.09
$k_{a,f}^{app}$ $((mg\,l^{-1})(mg\,l^{-1})^{-n}\,h^{-1})^a$	0.0081 ± 0.0026	0.0096 ± 0.0019	0.0081 ± 0.0019
$k_{d,f}$ $(h^{-1})^a$	0.017 ± 0.002	0.018 ± 0.001	0.027 ± 0.002
n^b	0.78	0.78	0.78
$E_{a,l}^{act}$ $(kJ\,mol^{-1})^b$	26	26	26
$E_{d,l}^{act}$ $(kJ\,mol^{-1})^b$	26	26	26
$E_{a,f}^{act}$ $(kJ\,mol^{-1})^b$	59	59	59
$E_{d,f}^{act}$ $(kJ\,mol^{-1})^b$	67	67	67
k_{deg}^{app} $(h^{-1})^c$	0.57 ± 0.08	0.43 ± 0.07	0.63 ± 0.08
k_{inact} $(h^{-1})^c$	0.18 ± 0.03	0.16 ± 0.03	0.21 ± 0.03
$C_{aq,t=o}$ $(mg\,l^{-1})^{c,d}$	0.41 ± 0.04	0.49 ± 0.05	0.39 ± 0.04

[a] Fitted parameters obtained from desorption experiment.
[b] Parameters used in sorption model and sorption-degradation model.
[c] Fitted parameters obtained from degradation experiments in the absence of soil.
[d] Not used in sorption-degradation model.

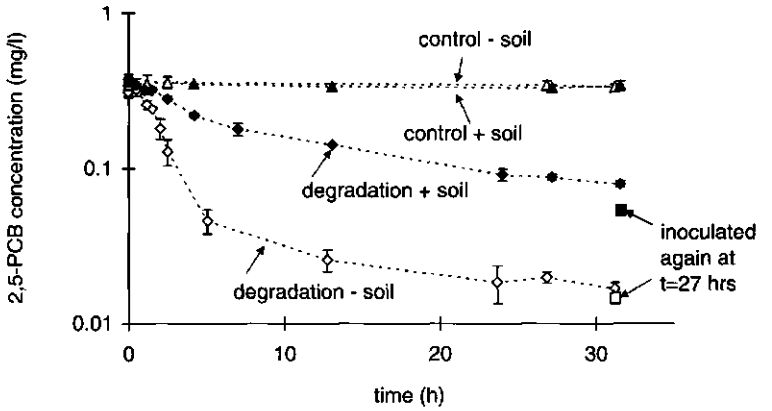

FIGURE 5.2. Measured degradation of 2,5-PCB in the presence (closed symbols) and absence (open symbols) of the sieve fraction < 0.5 mm of Wageningen Eng soil (experiment A). Control experiments were not inoculated (triangles). To some batches a second inoculation was added after 27 hrs (squares). Error bars represent standard deviations but may be obscured by the symbol.

Freundlich compartment of the sieve fraction < 0.063 mm was significantly larger compared to the other two fractions. The calculated average distribution of 2,5-PCB over the aqueous phase, the linear compartment and the non-linear compartment at the start of the desorption was $0.13 : 0.78 : 0.10$ for the three soil fractions. The modelling showed that after an adsorption period of 14 days at 4 °C, the majority of the total initial 2,5-PCB concentration was bound to the fast adsorbing and desorbing compartment and that the amount bound to the slow desorbing fraction was 10% of the total 2,5-PCB concentration and 13% of the total bound concentration. Prolonged contact time would have resulted in a larger slow desorbing fraction.

Experimental Results Degradation Kinetics

Degradation of 2,5-PCB in the absence and presence of different sieve fractions of Wageningen Eng soil are shown in Figures 5.2, 5.3, and 5.4. No removal of 2,5-PCB was observed in the controls without strain JHK. This indicates that removal of 2,5-PCB in the samples with strain JHK could only be ascribed to degradation by strain JHK. For each sieve fraction, the activity of strain JHK was determined by following the degradation in the absence of soil. The microbial activity in experiment A (Figure 5.2) and C (Figure 5.4) are relatively similar, but 2,5-PCB degradation in the

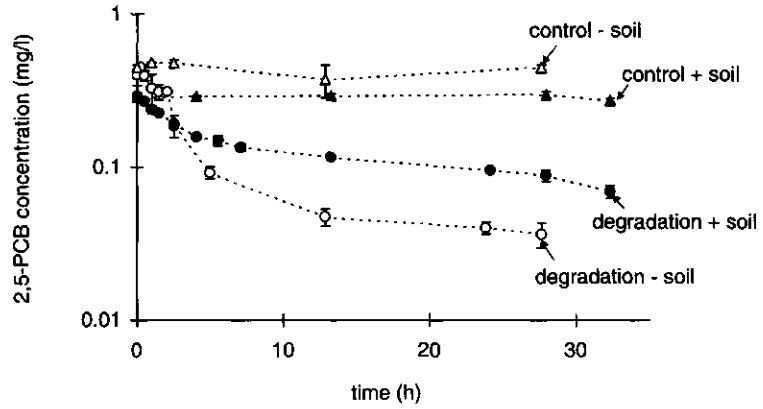

FIGURE 5.3. Measured degradation of 2,5-PCB in the presence (closed symbols) and absence (open symbols) of the sieve fraction 0.125–0.25 mm of Wageningen Eng soil (experiment B). Control experiments were not inoculated (triangles). Error bars represent standard deviations but may be obscured by the symbol.

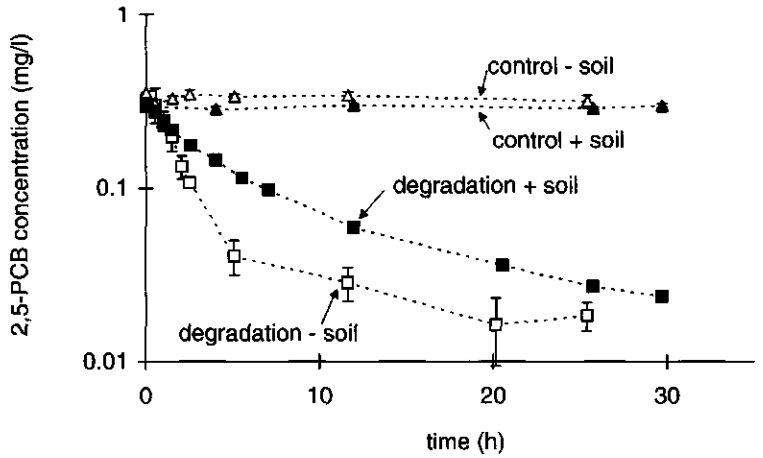

FIGURE 5.4. Measured degradation of 2,5-PCB in the presence (closed symbols) and absence (open symbols) of the sieve fraction < 0.063 mm of Wageningen Eng soil (experiment C). Control experiments were not inoculated (triangles). Error bars represent standard deviations but may be obscured by the symbol.

absence of soil in experiment B (Figure 5.3) is significantly slower. This implies that due to differences in microbial activity, the degradation in the presence of soil is not necessarily characteristic of the desorption kinetics of a soil fraction. However, for all fractions, the influence of the sorption of 2,5-PCB to the soil was clearly demonstrated by the significantly slower degradation.

Measured degradation in the absence of soil was biphasic and the 2,5-PCB concentration decreased only very slowly after an incubation period of 20 hours. It was expected that for the used experimental set-up, degradation would follow first-order kinetics which would result in a linear curve on log scale, see e.g. [58]. Microbial degradation can be described with first-order kinetics when substrate concentrations are below the half-saturation constant, and when the number of micro-organisms is constant. These prerequisites were met in our experimental set-up, see e.g. [2]. The decrease in degradation rate in the batches without soil could be caused by inactivation or death of the cells. If cells were inactivated during the degradation experiment, a second inoculation after a certain incubation period should result in additional degradation compared to the batches without a second inoculation. This was done in experiment A (Figure 5.2), for batches in the absence and presence of soil. Several batches were inoculated a second time at 27 hours after the first inoculation. Degradation in these batches was stopped at the end of experiment A at 32 hours. The second inoculation after 27 hours resulted in a significantly lower residual 2,5-PCB concentration at the end of the experiment in the presence of soil. For degradation in the absence of soil, the second inoculation did also result in additional degradation but the effect was small. These results do indeed suggest that inactivation of the cells occurred.

Inactivation or death of cells can occur when the supply rate of substrate is insufficient for maintenance requirements [75], when an essential nutrient or other compound, e.g. O_2, has become limiting, or when toxic compounds are present or formed. Since the incubations were performed in mineral medium and since the head-space and water volume should have contained enough oxygen for the complete degradation of the 2,5-PCB present, we believe that these factors did not limit the degradation. Preliminary experiments and studies indicated that *Pseudomonas* sp. strain JHK transforms 2,5-PCB into 2,5-dichlorobenzoate [35]. However, a chlorocatechol could have been formed in minor, toxic, quantities and toxic products could also have been formed through autooxidation of the catechol [35, 36]. The formation of a toxic compound could explain why the second inoculation had a more profound effect in the presence of soil than in the absence of soil.

With less 2,5-PCB degraded, less toxic product will be present in batches with soil while toxic products may also sorb to soil particles and become unavailable for strain JHK.

Modelling Degradation Kinetics

Preliminary modelling of 2,5-PCB degradation in the absence of soil showed that a first-order model was only capable of describing the initial degradation rate (data not shown). This corresponds with the proposed inactivation since that would not be observed in the first hours after inoculation. Paris et al. [58] described the microbial degradation of an organic compound with the following second-order kinetics model:

$$\frac{dC_{\mathrm{aq}}}{dt} = -k_{\mathrm{deg}} B C_{\mathrm{aq}}, \tag{5.4}$$

where B is the concentration of bacteria (cells l^{-1}) and k_{deg} ($\mathrm{l\,cells^{-1}\,h^{-1}}$) the second-order degradation rate constant. They showed that at constant bacterial concentrations, compound degradation was first-order and that pseudo-first-order rate constants were proportional to bacterial concentrations. Inactivation or death can now be taken into account by using an expression for the change of bacteria in time. For inactivation or death of micro-organisms the following first-order equation is used [23]:

$$\frac{dB}{dt} = -k_{\mathrm{inact}} B, \tag{5.5}$$

where k_{inact} (h^{-1}) is the first-order inactivation rate constant. If the rate expression is given a positive sign, the expression describes microbial growth. An analytical solution for equations 5.4 and 5.5 is:

$$C_{\mathrm{aq}} = C_{\mathrm{aq,t=0}}\, e^{-\frac{k_{\mathrm{deg}}^{\mathrm{app}}}{k_{\mathrm{inact}}}\left(1-e^{-k_{\mathrm{inact}}t}\right)}, \tag{5.6}$$

where

$$k_{\mathrm{deg}}^{\mathrm{app}} = k_{\mathrm{deg}} B_{\mathrm{t=0}}. \tag{5.7}$$

Due to relatively large variations in measured 2,5-PCB concentrations in the first hour of each degradation experiment, the initial concentration ($C_{\mathrm{aq,t=0}}$) was used as an additional fitting parameter. The rate constants, $k_{\mathrm{deg}}^{\mathrm{app}}$ and k_{inact}, and $C_{\mathrm{aq,t=0}}$ were fitted to the experimental data with equation 5.6 using a least-squares criterion.

The fitted degradation of 2,5-PCB in the absence of soil for each soil experiment is shown in Figure 5.5 and the fitted rate constants for degradation in the absence of soil are given in Table 5.1. The used model gives a good description of the degradation data. The fitted rate constants show

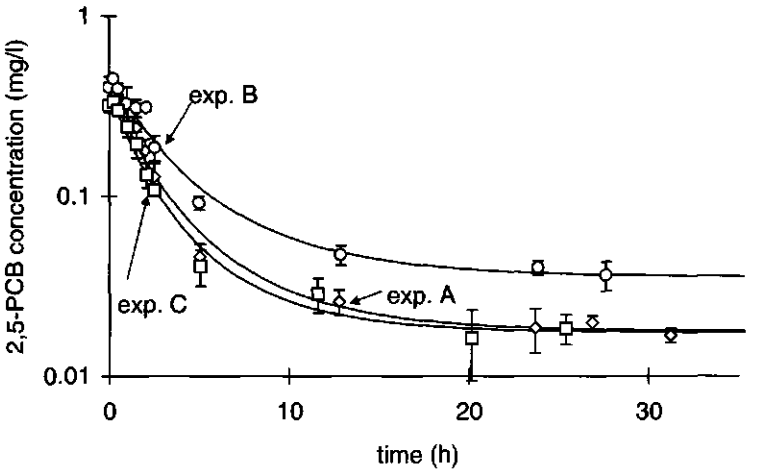

FIGURE 5.5. Measured and fitted degradation of 2,5-PCB in the absence of soil for experiments A (diamonds), B (circles) and C (squares) as given in Figures 5.2, 5.3, and 5.4. Solid lines are obtained with degradation model.

that the inactivation rate constant is not significantly different for the three experiments. The values of the apparent degradation rate constants are very similar to the desorption rate constants of the fast desorbing compartment of the three fractions. This implies that both equilibrium sorption and desorption kinetics could be important. Equilibrium sorption to the fast desorbing compartment can influence degradation in soil since part of the 2,5-PCB present is shielded from the micro-organisms. Desorption rate constants of the slow desorbing compartment are smaller than the fitted degradation rate. Degradation will therefore be faster than desorption from the slow desorbing compartment, and desorption kinetics of the slow desorbing compartment can therefore limit degradation in soil.

To predict degradation in the presence of soil, the differential equations describing, sorption, desorption, and degradation kinetics have to be coupled. With the assumption that only aqueous PCB can be degraded, equation 5.3 of the sorption model becomes

$$\frac{dC_{\mathrm{aq}}}{dt} = k_{\mathrm{d,f}} q_{\mathrm{f}} S + k_{\mathrm{d,l}} q_{\mathrm{l}} S - k_{\mathrm{a,f}}^{\mathrm{app}} C_{\mathrm{aq}}^{n} - k_{\mathrm{a,l}}^{\mathrm{app}} C_{\mathrm{aq}} - k_{\mathrm{deg}} B C_{\mathrm{aq}}. \qquad (5.8)$$

Equations 5.1, 5.2, 5.5, and 5.8 form the sorption-degradation model. This set of differential equations was solved with the method used for the sorption model. Since in both the desorption and the degradation experiments

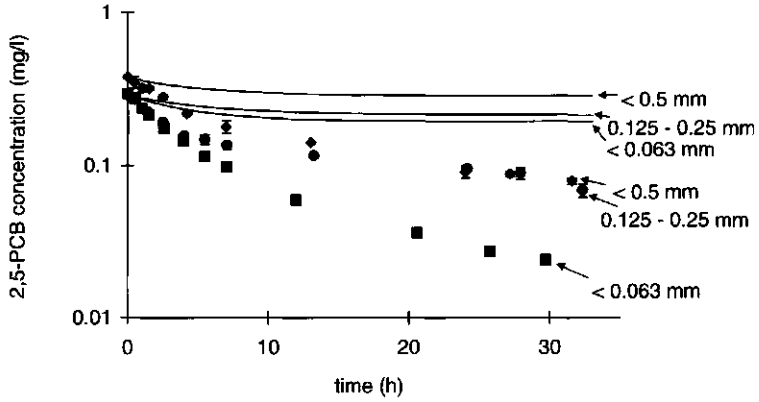

FIGURE 5.6. Measured and predicted degradation of 2,5-PCB in the presence of different sieve fractions of Wageningen Eng soil. Measured data are represented by symbols; < 0.5 mm (diamonds), 0.125–0.25 mm (circles) and < 0.063 mm (squares) and are also given in Figures 5.2, 5.3, and 5.4. Solid lines are predictions obtained with the sorption-degradation model.

identical soil suspensions were used, the adsorption and desorption rate constants can be used without prior normalisation. Furthermore, the simulations indicated that $B_{t=0}$ could be included in k_{deg} which allowed us to use k_{deg}^{app}. The predicted degradation in the presence of soil is shown in Figure 5.6, the values of the used rate constants are given in Table 5.1. The predicted curves do not describe the measured degradation of 2,5-PCB in the soil suspensions. Although our assumption that coupling measured desorption kinetics to measured degradation kinetics could describe measured degradation in the presence of soil could not be proven, it is interesting to speculate on possible reasons for the observed underestimation of the measured degradation rates in soil. Possible explanations are (1) desorption behaviour of 2,5-PCB in the incubations differs from the measured desorption kinetics in the gas-purge experiments, (2) strain JHK is more active in the soil incubations than in the incubations without soil, and (3) strain JHK is able to utilise bound substrate. These explanations are further discussed.

(1) The underestimated degradation in soil suggests that more substrate is available for the bacteria than predicted. This could occur when sorption and desorption kinetics are not described correctly. However, we do not expect that the observed underestimation is a result of the used model or the way desorption kinetics were measured. The description of

the measured desorption kinetics of 2,5-PCB from soil was good and the predictive capability of rate constants obtained with the gas-purge method has been demonstrated before [8, 70]. Sorption of bacteria to the surface of the soil particles has been used to explain increased desorption rates [31, 67]. Sorbed bacteria can steepen the concentrationgradients out of soil particles by removal of dissolved compound. However, since desorption is not the rate-limiting factor for the majority of bound 2,5-PCB in our experiments, this process cannot explain the underestimation of the measured desorption curves. Since strain JHK transforms 2,5-PCB into 2,5-dichlorobenzoate and since the latter has a good solubility in water, is less hydrophobic than 2,5-PCB, and is present at equally low concentrations as 2,5-PCB, it is not expected that 2,5-dichlorobenzoate can have a competitive effect on the desorption kinetics of 2,5-PCB. Production of biosurfactants can also increase desorption rates [37, 54, 88], but since desorption rates are not rate-limiting for the majority of bound 2,5-PCB, biosurfactants cannot explain the observed underestimation. (2) Micro-organisms could be more active in soil due to adsorption of toxic compounds to soil particles and their subsequent removal from the aqueous phase. Activation of micro-organisms could also be caused by the introduction of an additional carbon source or additional minerals and trace-elements originating from the soil. (3) When micro-organisms are able to remove directly bound substrate more substrate will be available for the bacteria than predicted. Guerin and Boyd [30] described differences in the bioavailability of soil-sorbed naphtalene for two bacterial species of which one species was able to use sorbed naphtalene.

Explanations (2) and (3) seem both possible in our experimental set-up. We therefore performed further modelling to see whether the data support one of the two explanations. To test whether strain JHK was more active in the batches with soil than in batches without soil, $k_{\mathrm{deg}}^{\mathrm{app}}$ and k_{inact} were fitted to the measured degradation in the presence of soil with the sorption-degradation model using equations 5.1, 5.2, 5.5, and 5.8. Parameters describing the sorption and desorption kinetics of 2,5-PCB were identical to the ones given in Table 5.1. To test whether strain JHK can utilise bound substrate, equation 5.2 can be rewritten as follows:

$$\frac{dq_{\mathrm{l}}S}{dt} = -k_{\mathrm{d,l}}q_{\mathrm{l}}S + k_{\mathrm{a,l}}^{\mathrm{app}}C_{\mathrm{aq}} - k_{\mathrm{deg,l}}Bq_{\mathrm{l}}S, \tag{5.9}$$

where $k_{\mathrm{deg,l}}$ ($\mathrm{l\,cells^{-1}\,h^{-1}}$) is a degradation rate constant specifically for the linear compartment. Since it is expected that only a certain part of the amount of bound 2,5-PCB can be used by strain JHK, $k_{\mathrm{deg,l}}$ can include a factor that is characteristic for the fraction of q_{l} that can be used by strain JHK. Since additional substrate degradation could result in less inactivation

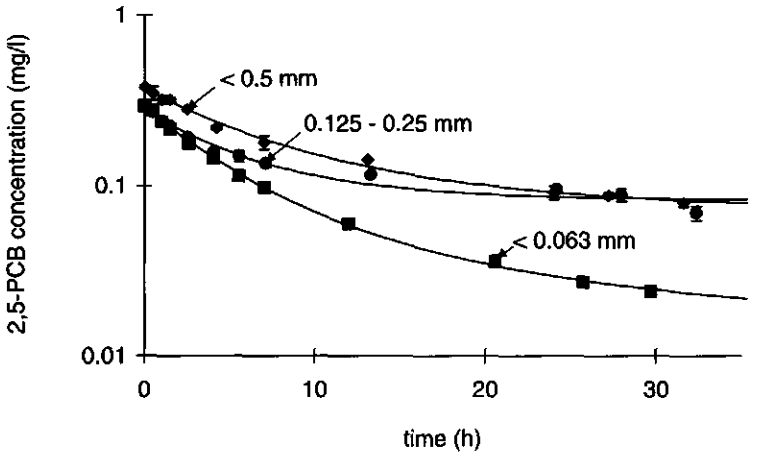

FIGURE 5.7. Measured and fitted degradation of 2,5-PCB in the presence of different sieve fractions of Wageningen Eng soil. Measured data are represented by symbols; < 0.5 mm (diamonds), 0.125–0.25 mm (circles) and < 0.063 mm (squares) and are also given in Figures 5.2, 5.3, and 5.4. Solid lines are fits obtained with the modified sorption-degradation model (eqs. 5.1, 5.5, 5.8, and 5.9).

$k_{\mathrm{deg,l}}^{\mathrm{app}}$ ($k_{\mathrm{deg,l}}^{\mathrm{app}} = k_{\mathrm{deg,l}} B_{\mathrm{t=0}}$) and k_{inact} were fitted to the measured degradation in the presence of soil using equations 5.1, 5.5, 5.8, and 5.9. Degradation from the aqueous phase was still described with $k_{\mathrm{deg}}^{\mathrm{app}}$ as given in Table 5.1.

Both fitting procedures gave identical fits of the data. Therefore, only the fitted degradation in the presence of soil with the modified sorption-degradation model (eqs. 5.1, 5.5, 5.8, and 5.9) is given in Figure 5.7. The fitted rate constants from both fitting procedures are given in Table 5.2. The fitting procedures show that it does not seem to matter whether the micro-organisms are more active or whether the micro-organisms are able to use bound substrate. The fitted inactivation rate constants in the presence of soil are smaller than in the absence of soil. The second inoculation in experiment A (Figure 5.2) also showed significantly more additional degradation in the presence of soil than in the incubations without soil. This suggests that transformation of 2,5-PCB by strain JHK may result in the formation of small amounts of a toxic compound. Since in the incubations without soil more 2,5-PCB was degraded, more toxic product can be formed while toxic products may also sorb to soil particles and become unavailable for strain JHK.

TABLE 5.2. Parameters Fitted to Measured Degradation in Soil

	sieve fraction < 0.5 mm (experiment A)	sieve fraction 0.125–0.25 mm (experiment B)	sieve fraction < 0.063 mm (experiment C)
$k_{\text{deg}}^{\text{app}}$ $(\text{h}^{-1})^a$	1.8 ± 0.1	2.2 ± 0.4	2.13 ± 0.08
k_{inact} $(\text{h}^{-1})^a$	0.078 ± 0.009	0.14 ± 0.02	0.054 ± 0.004
$k_{\text{deg,l}}^{\text{app}}$ $(\text{h}^{-1})^b$	0.10 ± 0.01	0.16 ± 0.02	0.146 ± 0.006
k_{inact} $(\text{h}^{-1})^b$	0.068 ± 0.007	0.12 ± 0.02	0.038 ± 0.003

[a] Fitted microbial degradation parameters (using eqs. 5.1, 5.2, 5.5, and 5.8), other parameters in the sorption-degradation model were identical to the parameters given in Table 5.1.

[b] Micro-organisms are able to use bound substrate (using eqs. 5.1, 5.5, 5.8, and 5.9), other parameters in the sorption-degradation model were identical to the parameters given in Table 5.1.

The measured degradation experiments in the presence of the different sieve fractions of Wageningen Eng soil showed that 10% of the initial amount of 2,5-PCB present was not or only very slowly degraded. The residual concentration in these experiments could be caused by inactivation of strain JHK or by rate-limiting desorption of 2,5-PCB from the slow desorbing compartment. For the fast desorbing compartment, the desorption rates of 2,5-PCB from soil were not rate-limiting for the degradation of 2,5-PCB in soil, but equilibrium sorption of 2,5-PCB to the fast desorbing compartment resulted in significantly slower removal rates. The experiments and modelling show that the presence of soil can have several effects on the microbial population and on the interactions between desorption kinetics and degradation kinetics. Laboratory measurements of degradation with (isolated) bacterial strains in the absence of soil may therefore not give an accurate estimate of the microbial activity in the field. To predict degradation of contaminants in the field reliable estimates are needed. Degradation in the presence of soil cannot be used to determine the intrinsic microbial activity independently since degradation will be influenced by sorption of the chemical.

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CHAPTER 6

Summary and Discussion

The objective of the study presented in this thesis is to investigate the desorption behaviour of organic contaminants in soil in regard to their microbial degradation. Knowledge of the factors that influence the release rates of organic contaminants in soil may lead to identify possible successful (and less expensive) remediation methods.

SOIL ORGANIC MATTER AND ORGANIC CONTAMINANTS

Natural organic matter in soils plays a dominant role in the sorption of organic contaminants to the soil. The affinity of organic matter for organic contaminants has resulted in the widespread use of organic carbon based partition coefficients to describe equilibrium sorption of organic contaminants to soils. Organic matter is a very heterogeneous and complex mixture of macromolecules and has been operationally divided into fulvic acids, humic acids, and humin. The affinities of these fractions for organic contaminants are largely controlled by particle size and polarity and have been shown to increase in the order fulvic acids > humic acids > humin [17, 27, 28]. The affinity of humin for pentachlorobenzene is indeed higher than the affinity of humic acids but also higher than the affinity of the soil from which the humin was derived (Chapter 4). The increased affinity of humin is correlated with slower sorption and desorption kinetics; the release rates of pentachlorobenzene from humin are slower than release rates from both soluble and adsorbed humic acids (Chapter 4).

The kinetics of the interactions between organic contaminants and organic matter are influenced by the three-dimensional structure of organic matter. For fulvic acids and humic acids, the effect of changes in the three-dimensional structure is relatively small since these particles are rather small. Swelling and shrinking of humin particles however, has a large effect on both the affinity for organic contaminants and the desorption kinetics (Chapter 4). Shrinking decreases the capacity of humin for contaminants but it also results in a more restricted and therefore slower desorption.

Sorption of pentachlorobenzene to the humic acids studied is non-linear, indicating that relatively more pentachlorobenzene is bound at low pentachlorobenzene concentrations than at high pentachlorobenzene concentrations (Chapter 2). This sorption behaviour suggests that it is more correct to refer to an adsorption process for the sorption of organic contaminants to humic acids than to refer to a partitioning process. The kinetic experiments with pentachlorobenzene and humic acids demonstrate the presence of a large fast desorbing fraction and a small slow desorbing fraction (Chapter 2). The slow desorbing fraction is proposed to result from a change of conformation of the humic acid after the binding of pentachlorobenzene. This structural change leads to entrapment of pentachlorobenzene within the humic acid structure.

Non-linear sorption behaviour has been observed in the literature for the interactions between many organic contaminants and soils [16, 29, 39, 40, 85]. This non-linear sorption behaviour has been correlated to the geological age of soil samples which corresponds with an increase of condensed and chemically reduced organic matter [39, 85]. This suggests that non-linear sorption behaviour can be caused predominantly by the interactions of the contaminant with the humin fraction. Sorption sites with a high sorption energy are formed when organic contaminants interact at multiple points with organic matter, when there is steric hindrance to desorption or adsorption e.g. in ink-bottle shaped cavities, or when the sorption of an organic contaminant induces a change in the organic matter structure [62]. The latter is proposed to cause the slow desorption of pentachlorobenzene from humic acids. The slow desorbing fraction in the interrupted flow experiment with humic acids could not be described with the sorption model that could describe the interrupted flow experiment with soil (Chapter 2 and Chapter 3). This suggests that the proposed sorption induced conformational change of humic acids plays only a minor role in the sorption behaviour of the soil. Whether sorption sites with a high sorption energy are formed as a result of multiple interactions of an organic contaminant with organic matter, or whether steric hindrance to desorption or adsorption plays a dominant role in the non-linear sorption of organic contaminants to soil and humin remains to be studied.

The observed desorption kinetics of pentachlorobenzene from humin indicate that humin plays a dominant role in the sorption behaviour of the soil (Chapter 4). A kinetic model that describes the sorption behaviour of pentachlorobenzene from Wageningen Eng soil was used to simulate the

influence of the humin fraction on the sorption behaviour of the soil (Chapter 4). The results of this simulation also indicate that humin is an important factor in the sorption behaviour of soils. However, a higher humin content did not result in slower desorption of the contaminant from the soil (Chapter 5), suggesting that the nature and three-dimensional structure of the humin is at least as important as the humin content. This has important implications for soils or sediments with a low organic carbon content, where a small amount of condensed and chemically reduced organic matter can have a large effect on the release rates of organic contaminants.

DESORPTION AND DEGRADATION OF ORGANIC CONTAMINANTS IN SOIL

The desorption rate of the slow desorbing fraction can be the rate-determining step in the degradation of organic contaminants in soil (Chapter 5). The influence of the slow desorbing organic contaminant fraction however, will depend on its magnitude. Since this fraction has slow adsorption and slow desorption rates, equilibration of this fraction is slow. This indicates that with increasing contact time, organic contaminants will be more strongly bound to the soil and subsequent degradation will be slower. Furthermore, due to the non-linear sorption behaviour of the slow desorbing contaminant fraction, equilibration will be faster at high organic contaminant concentrations (Chapter 3). This has implications for the field where a soil or sediment may only be exposed to a given chemical for a limited period of time but at a high concentration.

Degradation of 2,5-dichlorobiphenyl (2,5-PCB) by *Pseudomonas* sp. strain JHK in presence of different sieve fractions of a soil was predicted using measured desorption kinetics of 2,5-PCB from the different sieve fractions and measured degradation kinetics in absence of soil (Chapter 5). The predicted degradation of 2,5-PCB in the different soil suspensions underestimated measured degradation rates. This was probably caused by a higher activity of the bacteria in the batches with soil compared to the batches without soil. Laboratory measurements of degradation with (isolated) bacterial strains in the absence of soil may therefore not give an accurate estimate of the microbial activity in the field. To predict degradation of contaminants in the field reliable estimates are needed. Degradation in the presence of soil cannot be used to determine the intrinsic microbial activity independently since degradation will be influenced by sorption of the chemical.

IMPLICATIONS FOR REMEDIATION OF CONTAMINATED SOILS

To be able to conclude whether desorption kinetics are important in the in situ bioremediation of contaminated soils, the rate-determining step of degradation in soil has to be compared to the time-scale of a remediation project. Degradation of a fast desorbing contaminant fraction may be limited by the intrinsic microbial activity of degrading micro-organisms (Chapter 5). Remediation of a contaminated soil can then be enhanced by improving the environmental conditions for microbial degradation. In contaminated soils, contaminants may also be present as pure product or as a separate phase, the latter is referred to as non-aqueous phase liquids (NAPLs). In that case, the rate of dissolution of a contaminant from pure product or from the liquid phase can influence or control biodegradation. This study is especially relevant for the final stages of remediation when pure product has been removed. For degradation of the slow desorbing organic contaminant fraction in soil, the slow desorption rates can be rate-limiting (Chapter 5).

The time scale of a rate-determining step can be characterised by its half-life. In the case of first-order kinetics, the half-life of a reacting compound is independent of concentration and is given by $0.693/k$, see e.g. [72]. For non-linear kinetics, as is the case for the sorption of organic contaminants, the half-life depends on the concentration of the reacting compound and it is therefore not a constant. The half-life of a non-linear reacting system may easily be doubled with increasing non-linearity. Especially the last stages of desorption, when concentrations are low, become increasingly slower in case of non-linear sorption [20]. Although the use of a half-life for a rate constant of a non-linear reaction is debatable, it can be used as a lower limit. The slow desorption rate constant of pentachlorobenzene from the soil studied was $0.038\,\mathrm{day}^{-1}$ ($0.0016\,\mathrm{h}^{-1}$, Chapter 3), this results in a "half-life" of sorbed contaminant of 18 days. It indicates that when the time-scale of an in situ remediation of a contaminated soil is smaller than several months, slow desorption kinetics have to be taken into account.

Methods that can reduce the time scale of desorption can be used to enhance remediation of contaminated soils. Remediation at elevated temperatures can increase the desorption of organic contaminants [19, 84], but this may be too expensive in practice. Another possible method is the addition of a compound that influences the desorption behaviour of organic contaminants. Compounds tested in laboratory experiments include dissolved organic matter [42, 47], microbially produced cyclodextrin [12], organic co-solvents [5, 13, 41], chemically produced surfactants [22, 56, 60, 79, 86] and biologically produced surfactants [37, 54]. These compounds are usually

seen as a third retention "phase" for contaminants that reduces the amount of contaminants bound to the soil and concomitantly increases the contaminant concentration in the aqueous phase [12]. Based on the influence of organic matter on the sorption behaviour of organic contaminants in soil, only compounds that can influence the structure and nature of humin are expected to be able to increase desorption from the slow desorbing fraction. The effect of co-solvents on desorption rates has been attributed to the swelling of the organic matter matrix [13]. A biodegradable co-solvent as methanol may form an accepted treatment method when the co-solvent can be applied at relatively low concentrations. It has also been postulated that the influence of surfactants on the desorption kinetics of organic contaminants is related to surfactant-induced swelling of organic matter [22, 54, 86]. A disadvantage of the use of surfactants that are able to expand organic matter is that their effect is a result of the adsorption of the surfactants to soil organic matter. Therefore, care has to be taken in the selection of the surfactant since they may not be retrieved from the soil and sorbed surfactants may also resist degradation in the soil.

Since organic contaminants seem to be sequestered within the soil matrix, it has been suggested that contaminated soils do not have to be remediated or do not have to be remediated any further when the slow release rates of the contaminants hamper their microbial degradation. Organic contaminants that are not available for microbial degradation may also not be harmful for plants, animals and humans. It has also been suggested that since most soils show a natural capacity for removing organic contaminants via microbial degradation, this natural remediation capacity may be used to remediate a contaminated soil.

The simulations in which the influence of different purging strategies was demonstrated, indicated that after removal of the fast desorbing fraction, efficient removal may be obtained at very slow purging rates (Chapter 3). The simulations further showed that when the organic contaminant in the aqueous phase is not degraded anymore, the soil system will re-equilibrate and the contaminant concentration in the aqueous phase will increase. For natural remediation the question is whether micro-organisms that are already present in the soil, can cause a removal rate similar to the very slow purging rates in the simulations. When contaminant concentrations are very low, micro-organisms may not be able to use them as growth substrate but maintenance requirements of the micro-organisms can still be met. This will result in a slow but ongoing degradation of the contaminants. A further decrease of the contaminant concentration due to the slow release rates of the contaminant from the soil could result in concentrations

below the maintenance requirements and bacteria can subsequently die or enter a dormant state. The release rate of contaminants from the soil and the maintenance requirements of the micro-organisms will determine the residual organic contaminant concentration in the aqueous phase [7].

The importance of the residual aqueous and bound concentration for the environmental risk that a contaminated soil may form is something that cannot be dealt with easily. Direct or acute toxic effects will not be measured when the residual aqueous concentration is very low but negative effects on the long-run will be hard to determine. This is of importance since the contaminated soil may form a continuous source of low contaminant concentrations that can be transported to various parts in the soil system, such as air and groundwater. However, when micro-organisms are able to continuously degrade contaminants that become available after desorption, the natural degradation of organic contaminants in the soil can be a very cost-effective remediation method in the last stages of the in situ remediation of a contaminated soil. The need for continuous monitoring of such a contaminated soil is however evident.

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Samenvatting

De omvang van de bodemverontreiniging in Nederland is aanzienlijk. In het Nationaal Milieubeleidsplan van 1998 (NMP3) wordt geschat dat zo'n 175.000 locaties ernstig verontreinigd zijn. Voor 35% hiervan wordt sanering urgent geacht omdat de gezondheidsrisico's voor de mens, de risico's voor het ecosysteem of de verspreidingsrisico's te groot zijn. In het NMP3 is berekend dat honderd miljard gulden nodig is om alle vervuilde grond weer schoon te maken. Er is dan ook een grote vraag naar goedkopere en efficiëntere reinigingstechnieken.

Een mogelijke reinigingstechniek waarbij de grond niet afgegraven hoeft te worden is de afbraak van verontreinigingen door micro-organismen die van nature in de bodem aanwezig zijn. Bacteriën en schimmels zijn in principe in staat om veel verschillende typen organische verontreinigingen zoals PAK's (polyaromatische koolwaterstoffen) en PCB's (polychloorbiphenylen) af te breken. Zware metalen, die tot de anorganische verontreinigingen behoren, kunnen zij niet afbreken. De organische verontreinigingen blijken echter in de praktijk vaak niet, of slechts heel langzaam afgebroken te worden. Zelfs als de milieuomstandigheden optimaal zijn voor de micro-organismen, bij onder meer de juiste temperatuur, zuurgraad en zoutgehalte, is de afbraak heel traag. De verontreinigingen blijken niet te worden afgebroken omdat ze door hun sterke binding aan de bodem niet beschikbaar zijn voor de micro-organismen. De mate van binding van de organische verontreinigingen aan de bodem en de snelheid waarmee deze verontreinigingen weer vrij kunnen komen kunnen het succes van een bodemsanering bepalen.

In dit onderzoek is gekeken naar factoren die de binding en de desorptiesnelheid (vrijkomingssnelheid) van organische verontreinigingen in de bodem bepalen. Ook is het effect van de desorptiesnelheid op de microbiële afbraak van verontreinigingen in de bodem bestudeerd. Als modelverontreiniging zijn een gechloreerd benzeen, pentachloorbenzeen en het PCB 2,5-dichloorbiphenyl gebruikt. Het is bekend dat de organische stof in de bodem een belangrijke rol speelt bij de binding van verontreinigingen aan de bodem. Of organische stof ook een belangrijke rol kan spelen bij de desorptiesnelheid is echter nog niet duidelijk. Organische stof in de bodem

onstaat door afbraak en compostering van dode planten en dieren. Het is zeer belangrijk voor de vruchtbaarheid van een bodem. Door zijn ontstaanswijze bestaat organische stof uit een zeer complex en divers mengsel van grote moleculen. Organische stof kan onderverdeeld worden in verschillende fracties: fulvozuren, humuszuren en humine. Een belangrijk deel van dit onderzoek is gericht op het belang van organische stof voor de binding en desorptie van verontreinigingen in de bodem.

Uit dit onderzoek blijkt dat verschillende organische stoffracties in de bodem een verschillende affiniteit hebben voor pentachloorbenzeen en dat ze ook een verschillende desorptiesnelheid laten zien (Hoofdstuk 4). Humine laat een grotere affiniteit en een langzamere desorptie zien dan fulvozuren en humuszuren. Humine kan zelfs een bepalende factor zijn voor de binding en de desorptie van verontreinigingen in de bodem. Het bindingsgedrag van humine wordt sterk beïnvloed door de ruimtelijke structuur van de humine. Gedroogde humine heeft een dichte structuur. Daardoor wordt er minder pentachloorbenzeen opgenomen, maar wat er gebonden is komt er ook veel moeilijker uit (Hoofdstuk 4). Het tegengestelde gebeurt indien de humine "zwelt" en de structuur losser en ruimer wordt.

Het bindingsgedrag van pentachloorbenzeen aan humuszuren is niet-lineair (Hoofdstuk 2). Niet-lineair betekent dat bij lage concentraties verontreiniging relatief meer gebonden is dan bij hoge concentraties verontreiniging. Ook voor bodems is waargenomen dat organische verontreinigingen niet-lineair adsorberen. Dit heeft een grote invloed op de snelheid waarmee verontreinigingen vastgelegd worden in de bodemmatrix en op de snelheid waarmee ze kunnen desorberen (Hoofdstuk 3). Vooral de desorptie zal veel langzamer zijn bij een niet-lineaire binding.

Met behulp van de gemeten desorptiesnelheid van 2,5-dichloorbiphenyl uit een bodem en met de gemeten afbraaksnelheid door een bacterie zonder bodem, is de afbraaksnelheid van 2,5-dichloorbiphenyl in een bodem voorspeld (Hoofdstuk 5). Voor de uitgevoerde experimenten blijkt dat de voorspelde afbraaksnelheid in de bodem veel kleiner is dan de gemeten afbraaksnelheid. Het verschil tussen de gemeten en de voorspelde afbraaksnelheid kon verklaard worden door aan te nemen dat de bacteriën in de experimenten met bodem actiever zijn dan in de experimenten zonder bodem. Dit geeft aan dat het niet zonder meer mogelijk is om de afbraak in een bodem exact te voorspellen omdat de activiteit van de bacteriën in de bodem af kan wijken van de activiteit van bacteriën in laboratoriumexperimenten.

Uit de modelberekeningen blijkt dat, voor de afbraak van snel desorberend 2,5-dichloorbiphenyl, de bacterie de uiteindelijke afbraaksnelheid in

de bodem bepaalt. Dit betekent dat stimulering van de micro-organismen in de bodem de afbraak van snel desorberende verontreinigingen kan versnellen. Voor de afbraak van langzaam desorberend 2,5-dichloorbiphenyl bepaalt de desorptiesnelheid echter de uiteindelijke afbraaksnelheid in de bodem. Wanneer men de afbraak van langzaam desorberende verontreinigingen in een vervuilde bodem wil versnellen, dan kan men daarom zoeken naar methoden die het bindingsgedrag van humine veranderen. Stoffen die in de bodem gepompt kunnen worden en die de humine kunnen laten zwellen waardoor de desorptie wordt versneld, zijn oplosmiddelen zoals methanol en sommige zepen (surfactants). Of deze stoffen in de praktijk gebruikt kunnen worden hangt af van hun kosten en, indien ze in de bodem achter blijven, van hun giftigheid en hun effect op de bodem.

Doordat verontreinigingen zo langzaam uit de bodem desorberen is ook wel gesuggereerd dat men dan niet hoeft te saneren. Als de verontreiniging niet beschikbaar is voor micro-organismen, dan is de kans groot dat deze ook niet gevaarlijk is voor planten, dieren en mensen. Indien men niet actief saneert kan de afbraak van verontreinigingen door micro-organismen die van nature in de bodem aanwezig zijn in principe doorgaan. Alhoewel dit langzaam zal gaan, kan de zelfreinigende werking van de bodem zo gebruikt worden om de grond schoon te maken. Modelberekeningen geven aan dat de langzaam desorberende verontreinigingen efficiënt verwijderd kunnen worden bij een lage verwijderingssnelheid (Hoofdstuk 3). De vraag is nu of micro-organismen een lage verwijderingssnelheid in stand kunnen houden. Dit hangt af van de desorptiesnelheid van verontreinigingen. Indien de desorptiesnelheid van een verontreiniging zo laag is dat er te weinig verontreiniging vrijkomt voor de micro-organismen om van te kunnen leven, kan er een restconcentratie ontstaan in de waterfase van de bodem terwijl er nog wel vrij veel gebonden is. Dit betekent dat door desorptie de hoeveelheid verontreiniging in de waterfase weer aangevuld kan worden indien de concentratie verlaagd wordt door grondwaterstromingen of vervluchtiging. De bodem kan zo een bron van verontreinigingen worden waaruit langdurig geringe hoeveelheden verontreinigingen vrijkomen. Alhoewel de verontreinigingen slechts in geringe hoeveelheden vrijkomen, kunnen ze wel verspreid worden naar de lucht, het grondwater en naar een nog schone bodem. Wanneer de micro-organismen echter wel in staat zijn om langzaam desorberende verontreinigingen af te breken, dan kan de zelfreinigende werking van de bodem gebruikt worden als goedkope en efficiënte reinigingsmethode. Controle blijft echter wel noodzakelijk.

Levensloop

Wendela Schlebaum werd geboren op 12 augustus 1969 te Amsterdam. In 1987 behaalde zij het gymnasium-β diploma aan Het Waterlant-College te Amsterdam-Noord. Daarna studeerde ze moleculaire wetenschappen aan de Landbouwuniversiteit Wageningen. Haar studie rondde ze af met een afstudeervak kolloïdchemie, een afstudeervak bodemverontreiniging bij de Soil Science Department, Lincoln University te Lincoln in Nieuw Zeeland, een afstudeervak bodemverontreiniging bij het DLO-Staring Centrum te Wageningen en een stage bij Tauw te Deventer. In oktober 1993 begon zij als assistent in opleiding bij de vakgroep Bodemkunde en Plantenvoeding en bij de vakgroep Microbiologie. Sinds oktober 1998 werkt zij als onderzoeker bij de afdeling research & development van Tauw te Deventer.

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