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Fate of chlorinated dibenzo-p-dioxins and dibenzofurans in the soil-water-plant system

A preliminary model study

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ABSTRACT

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In order to study the effects of proposed techniques for rehabilitating the Lickebaert area for agricultural use, the TRANSOL model, describing transport of a solute in the soil, was extended to the FAD model, describing the fate of dioxins and furans in the soil-water-plant system. For lack of appropriate deposition data, the TRANSOL model instead of the FAD model was used to evaluate the measures proposed.

Keywords: fate, dioxin, furan, solute transport, simulation model

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PREFACE

This research on modelling the fate of chlorinated dibenzo-p-dioxins and dibenzofurans in the soil-water-plant system in order to evaluate the effects of technical interventions in this system has been initiated and supported by the Dutch Ministry of Agriculture, Nature and Fisheries.

I would like to thank Joop Kroes and Koen Roest for their advice during the preparation of this report.

SUMMARY

In order to study the effects of techniques proposed for rehabilitating the Lickebaert area for agricultural use, the fate of dioxins and furans in the soil-water-plant system had to be modelled. To do so, the TRANSOL model, describing transport of a solute in the soil, was extended to the FAD model. The fate of dioxins in the natural environment is influenced by the following processes: deposition, volatilization, photodegradation, plant uptake, ingestion of grass and intake of soil by cattle, infiltration, sorption, convection, diffusion, runoff, drainage and leaching, non-homogeneous transport, biodegradation, and mixing. The most important processes are included in FAD. As no appropriate deposition data became available, the FAD model could not be used for evaluating the measures proposed. Reduced equations, fully covered by the TRANSOL model, were used instead. Consequently, only the fate of dioxins and furans in the soil profile were studied.

Dioxins and furans are strongly adsorbed to the soil organic matter and appear almost immobile in the soil profile. Passive plant uptake is negligibly small. Also transport by leaching to the groundwater and by capillary rise can be neglected. All of the solutions proposed seem acceptable from an environmental point of view. As not all processes have been taken into account, the calculated results with the reduced model must be interpreted carefully and should be compared with the qualitative description resulting from the literature review (Van der Bolt, 1990).

1 INTRODUCTION

In order to assess the harmful effects on humans and other organisms the toxicities of (poly)chlorinated dibenzo-p-dioxins (PCDDs) and dibenzofurans (PCDFs) as well as the exposure to these compounds have to be studied. To gain insight into the exposure, both the amounts of dioxins and furans released to the environment and the fate of dioxins and furans in the environment have to be investigated.

In the Netherlands, recently high PCDD levels have been detected in milk from cows grazing in the Lickebaert area (Liem et al. 1989) and the Zaandam/Alkmaar region (De Jong et al. 1990). Sources of pollution are probably the nearby waste incinerators. Because of the large economic implications some technical solutions have been proposed to rehabilitate the Lickebaert area in order to save the present agicultural use (MLNV 1989).

To study the effect of the measures proposed on the pollution, the behaviour of the contaminant in the environment has to be known. In december 1989 the Ministery of Agriculture, Nature and Fisheries started a research programme that should result in an evaluation of the agricultural consequences and the environmental risk of the measures that were proposed in april 1990. The research was carried out by RIVM (monitoring the pollution), IVVO (studying the intake and excretion of dioxins by cows), IMAG (development of a specific plough), and SC (mapping the soil and evaluating the agricultural and environmental consequences of the interventions proposed).

This report describes the modelling of the processes that determine the fate of the dioxins and furans in the soil-water-plant system and the evaluation of the environmental effects of the measures proposed in the Lickebaert area by applying a simplified model. The study should be classified as preliminary because of the limited time available. As a consequence, the model-building activity was restricted and simplifications and assumptions had to be made. Based on the literature research done prior to this study (Van der Bolt 1990), a description of PCDDs and PCDFs and of the properties of these chemicals with respect to their environmental fate is given in Chapter 2. Chapter 3 contains a more detailed description of the elements and processes of this system and the representation of the processes in mathematical formulas. Finally, the equations covering the complete system and their implementation in a (Fortran) computer program are presented. In Chapter 4 the simplified equations are used to evaluate the environmental effect of the solutions proposed for the Lickebaert area.

The final recommendations on the technical solutions proposed, resulting from agricultural and environmental evaluations, are presented in a separate report by the Winand Staring Centre (Boels et al. 1990).

2 CHARACTERISTICS OF THE SYSTEM

2.1 Polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs)

(Poly)chlorinated dibenzo-p-dioxins and dibenzofurans are planar aromatic compounds with three hexagonical ringstructures. One to eight chlorine atoms can be attached, leading to 75 PCDD isomers and 135 PCDF isomers. Because of their similar structures (Fig. 1) PCDDs and PCDFs have comparable physical and chemical properties.

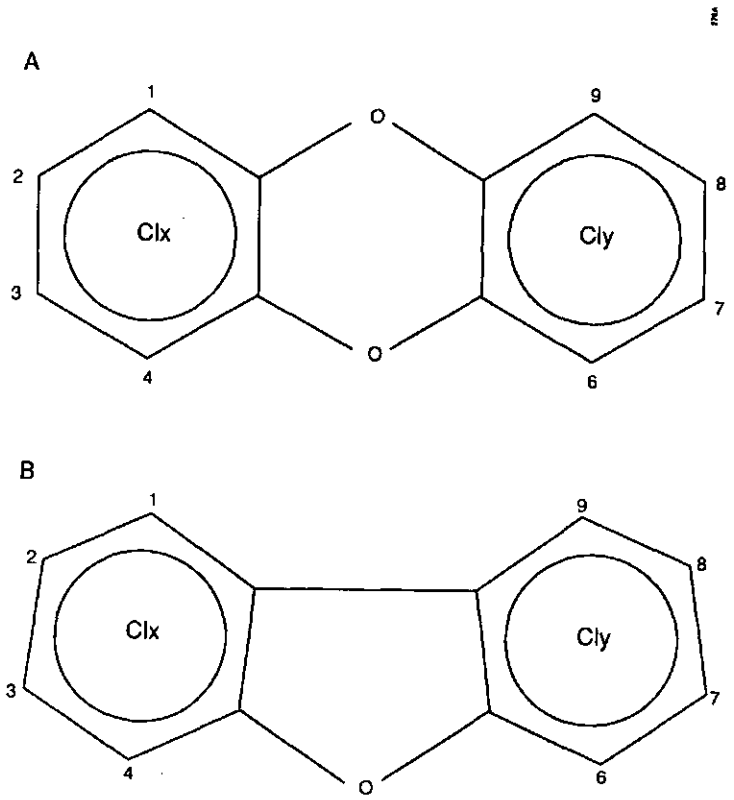


Figure 1 Structure of PCDDs and PCDFs.

PCDDs and PCDFs are nonpolar, lipophylic and chemically stable. Due to the lipophylicity the PCDDs and PCDFs are slightly soluble in water and adsorb strongly to soil organic matter. PCDDs and PCDFs are decomposed completely at temperatures above 800°C but can be degraded by photochemical reactions in presence of ultraviolet light. The properties of these compounds, including toxicity, depend on the degree of chlorination. As 2,3,7,8-tetrachloro-dibenzo-p-dioxin (TCDD) appeared to be the most toxic congener this isomer has been studied extensively and is often supposed to represent the complete group of PCDDs and PCDFs.

2.2 The fate of PCDDs and PCDFs in the environment

Environmental contamination with PCDDs and PCDFs can result from industrial and agricultural chemicals containing dioxins as impurities, from accidental formation and release into the environment, from incineration of industrial chemicals acting as precursors and by generation from suitable precursors under natural conditions. Also leaching from dump sites is a well known source of contamination. Formation of PCDDs and PCDFs under natural conditions is possible, but seems negligible as the rate of degradation exceeds the rate of formation. Chlorinated dioxins enter the environment as airborne particles or in solution. Newly formed PCDDs and PCDFs are gaseous and are subject to very rapid dechlorination. The non-photodegraded compounds cool down and precipitate at particles. Differences in photochemical decomposition-rates and volatilization rates determine the distribution between the precipitated isomers. The particles move downward due to gravity or will be washed out by rainfall and precipitate at the soil-surface, at the vegetation or in aqueous systems.

The PCDDs and PCDFs precipitated on plants are fast photodecomposed because of presence of organic hydrogen donors at the waxy leaf surfaces. Volatilization also may occur. In case of rainfall the compounds adsorbed to the plant surface may be washed off and drop to the soil surface. Consequently precipitation on plants can be regarded as an interception process, retarding and diminishing effective precipitation. The compounds present at the soil surface are subject to slow photodegradation of the pure chemicals without sensitizer as long as no organic solvents like oil or pesticides are present. Photolysis of the pure compounds on the soil surface does not follow first order kinetics because they are partly protected from irradiation by soil particles and because they are strongly sorbed to soil particles. In this part of the system (plants and soil surface) the PCDDs and PCDFs may be transported in horizontal direction by wind or by water.

The PCDDs or PCDFs remaining at the soil surface dissolve into water and leache downward. The lipophylic character of these compounds makes them very sensitive to adsorption to (organic) soil particles and downward transport will be retarded. For low water solubility and huge sorption leaching will be very small and the PCDDs and PCDFs appear immobile. Some of the organic matter is dissolved and can be transported downward, carrying the sorbed material. Diffusion due to concentration and temperature gradients leads to a slow redistribution of these chemicals in the soil profile and makes it neccessary to take both water and vapour phase into account. Volatilization losses due to the diffusion through the soil surface and the watermediated evaporation, are concentration dependent and decrease with increasing organic carbon content of the soil (due to sorption). The volatilized compounds are either photodegraded in gas phase or will be adsorbed to plants. Uptake and translocation by plants seem to be negligble, which holds also for microbiological degradation. In this part of the system there is no degradation of the contaminants. Redistribution of these compounds has to be studied in order to get insight into the escape by volatilization, uptake by plants and contamination of the aquifer. Preferent pathways, cracks and biological activity affect the distribution of

chemicals in the soil and may result in a faster downward movement of the pollutants, and consequently in the pollution of the groundwater.

Overall half-lives of these chemicals in the soil-water-plant system are determined by the processes at the surface, i.e. volatilization and photodegradation. Therefore measured half-lives after an incidental release vary from fast, immediately after contamination (as photodecomposition is dominant), to very slow after some months when volatilization becomes the main pathway of disappearance from the soil.

Grazing cows ingest grass and take in soil, thereby diminishing the amounts of dioxins and furans present at the soil surface and the vegetation. Because of the limited bioavailability of these compounds part of them is excreted with manure and in this way PCDDs and PCDFs return to the soil surface. Grazing by cattle leads to both a redistribution and a decrease of contamination on the vegetation and the soil surface. Through the consumption of milk and beef, legumes and drinking water humans are exposed to a possible contamination.

3 MODELLING THE FATE OF PCDDs AND PCDFs IN THE SOIL-WATER-PLANT SYSTEM

3.1 The soil-water-plant system

The system determining the fate of PCDDs and PCDFs in the environment as described in paragraph 2.2 has been schematised in Figure 2. A system consists of elements that are interrelated by processes. The elements discerned are: the source, the atmosferic load, the soil surface, the vegetation, the soil system and the cattle.

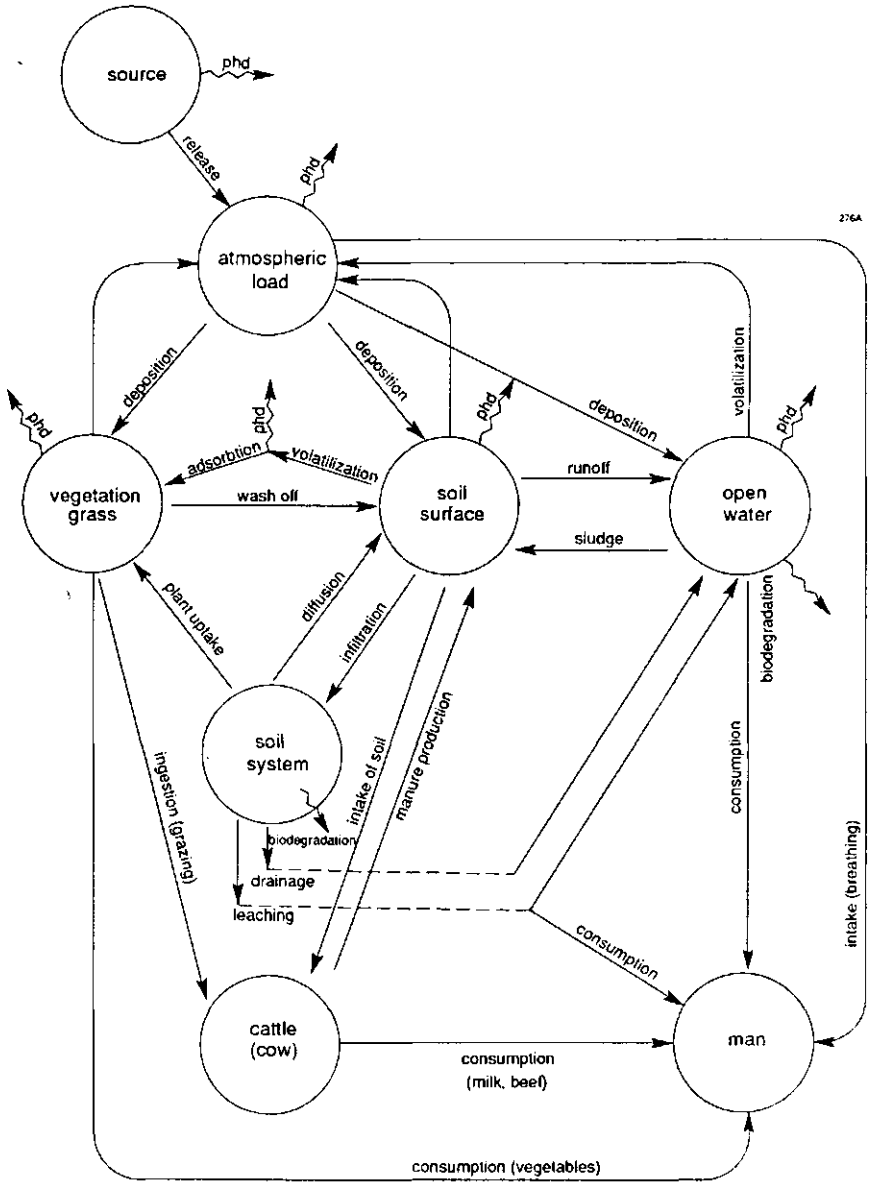


Figure 2 Schematization of the environmental system that determines the fate of the PCDDs and PCDFs after formation.

The elements open water and man were out of the scope of this project. For reasons of simplicity and as the relations dealing with the atmosferic load are one-directional, the atmosferic load will be assumed to be an input variable (efforts in modelling this part of the environmental system, i.e. release from the source till deposition, have been made by Townsend 1983 and Eduljee and Townsend 1987). The element cattle is considered to be an external element. Omitting the redistribution by manure excretion, the cattle acts as a sink of the pollutants. A system of three closely interrelated elements results: the soil-water-plant system. This system is given in Figure 3.

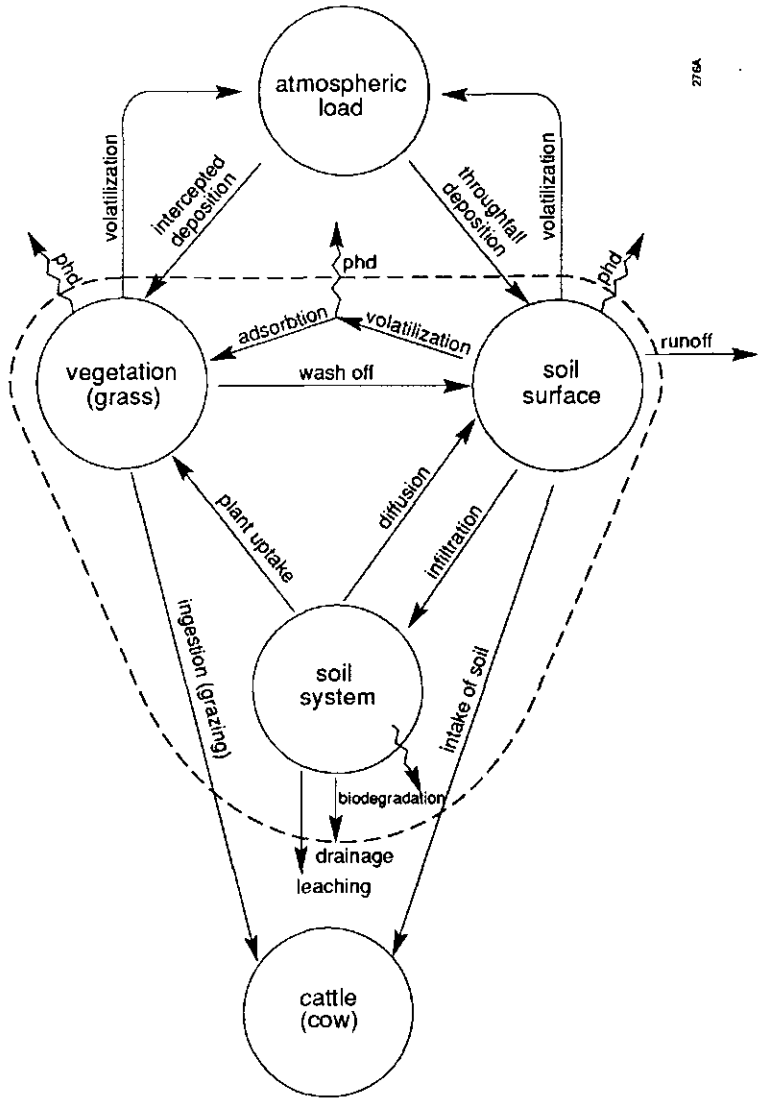


Figure 3 The soil-water-plant system with the elements and relations determining the fate of deposited PCDDs and PCDFs.

The system will be modelled pseudo-two dimensional. The relevant processes are treated in paragraph 3.2.

3.2 Processes in the soil-water-plant system

3.2.1 Deposition

Due to gravity (dry deposition) or washing out by rainfall (wet deposition) the airborne PCDDs and PCDFs will precipitate at the soil surface or at the covering vegetation. The partitioning of the pollutants between these two elements is represented in the model by a factor α which is equal to the ratio of the averaged amount deposited at the vegetation (D_v) and the averaged total deposited amount D. This empirical factor α describes the amount of deposition intercepted by the vegetation and has no physical meaning. The interception depends on the kind of vegetation, its growth stage, the soil cover, the intensity of rainfall etc. The interception and resulting deposition are calculated by:

$$D_v = \alpha * D \qquad (1a)$$

and

$$D_{ss} = (1-\alpha) * D \qquad (1b)$$

with

D_v	= vegetation deposition rate	[$kg_c\ m^{-2}\ d^{-1}$]
D_{ss}	= soil surface deposition rate	[$kg_c\ m^{-2}\ d^{-1}$]
α	= D_v / (D_v + D_{ss})	
	= fraction intercepted	[-]
D	= total deposited amount	[$kg_c\ m^{-2}\ d^{-1}$]

No quantitative data on wash off effects due to rainfall are available. The wash off effects are also covered by the empirical factor α. α is assumed to be identical for both dry and wet deposition.

3.2.2 Volatilization

Volatilization is treated as the mass-flux through the soil surface due to diffusion in the soil. Thereby volatilization depends on concentration gradients, temperature, organic carbon content, soil moisture content and capilary rise. In order to investigate the importance of volatilization as a path of dissipation of PCDDs and PCDFs from the soil into the atmosphere a simple formula has been derived (Appendix 1). Application of this formula to the Lickebaert area (Appendix 2) leads to the conclusion that volatilization for the Lickebaert area is of no importance (due to the high organic matter content of the soil), even on the long term. Therefore this process has not been included in the model.

3.2.3 Photodegradation

Although dioxins and furans are chemicaly stable, they decompose under the influence of ultraviolet light of wavelenghts that are part of the natural sunlight spectrum.

The photochemical degradation is described accurately by a first order reaction.

$$\left(\frac{dM}{dt}\right)_{Phd} = k * M \qquad (2)$$

with

$\left(\frac{dM}{dt}\right)_{Phd}$	= photodegradation rate	[$kg_c\ m^{-2}\ d^{-1}$]
M	= mass of chemical	[$kg_c\ m^{-2}$]
k	= reaction rate velocity	[d^{-1}]

The reaction rate velocity k is calculated from the half-life $t_{1/2}$:

$$k = \frac{\ln(2)}{t_{1/2}}$$

Half-lives of PCDDs and PCDFs are dependent on the phase of these chemicals (i.e. gas phase, solid phase or soluted) and on the presence of a proton donor.

3.2.4 Plant uptake

It is not known whether plant uptake of dioxins takes place. The available articles are contradictory; some of them confirm plant uptake whereas other studies deny plant uptake. Both possibilities have to be taken in account. Therefore plant uptake is described as a function of the transpiration flux and the concentration of the soil moisture:

$$\left(\frac{dM}{dt}\right)_{Upt} = q_t * C * r \qquad (3)$$

with

$\left(\frac{dM}{dt}\right)_{Upt}$	= plant uptake rate	[$kg_c\ m^{-2}\ d^{-1}$]
q_t	= transpiration flux	[$m\ d^{-1}$]
C	= concentration of soil moisture	[$kg_c\ m^{-3}$]
r	= regulation factor	[-]

The regulation factor determines the plant uptake. Four cases can be distinguished:

if	r = 0	no plant uptake,
if	0 < r < 1	uptake is reduced actively by plants,
if	r = 1	passive plant uptake, and
if	r > 1	preferential uptake by plants.

There is no uptake by leaf-surfaces after adsorption to the leafs. Adsorption depends on the composition of the cuticula of the plant surface (roots, leafs). Adsorption to roots is not incorporated in the model. Adsorption to leafs is taken into account by the factor α and is equal to the deposition at the vegetation.

3.2.5 Ingestion of grass and intake of soil by cattle

Reliable data on uptake and excretion of PCDDs and PCDFs by cattle are lacking. Research is carried out at this moment by IVVO. As soon as the results will be presented it will be possible to describe the fate of the PCDDs and PCDFs in the cattle system more detailed. At present only the ingestion of grass and intake of soil have been modelled.
Ingestion of dioxins and furans is calculated as follows:

$$\left(\frac{dM}{dt}\right)_{Ing} = \frac{nrc * M_v * I_v}{A_v} \qquad (4)$$

with

$\left(\frac{dM}{dt}\right)_{Ing}$	= ingestion rate of the chemical	[$kg_c\ m^{-2}\ d^{-1}$]
nrc	= number of grazing cows per m^2	[cows m^{-2}]
M_v	= mass of chemical at vegetation	[$kg_c\ m^{-2}$]
I_v	= daily ingestion of grass per cow	[$kg_v\ cow^{-1}\ d^{-1}$]
A_v	= amount of grass present	[$kg_v\ m^{-2}$]

The representation of the intake of the chemicals with soil is a problem. In the model this is assumed to occur from a soil surface reservoir. A soil surface reservoir is an imaginary layer at the top of the soil profile defined for calculation purposes. This layer contains the applied or deposited compounds that not yet have been infiltrated into the physical soil system. As a first approximation the ingestion of soil can be assumed to be constant. In this case the intake is independent on the amounts of the chemicals deposited at the soil surface. In order to relate the intake of soil to the amounts of chemicals present at the soil surface, the intake is calculated analogeous to ingestion of grass by:

$$\left(\frac{dM}{dt}\right)_{Int} = \frac{nrc * M_{ss} * I_s}{A_s} \qquad (5a)$$

with

$\left(\frac{dM}{dt}\right)_{Int}$	= intake of chemical with soil	[$kg_c\ m^{-2}\ d^{-1}$]
M_{ss}	= mass of chemical at soil surface	[$kg_c\ m^{-2}$]
I_s	= a * I_v	
	= intake of soil per cow per day	[$kg_s\ cow^{-1}\ d^{-1}$]
a	= intake of soil per intake of grass	[$kg_s\ kg_v^{-1}$]
A_s	= amount of soil per square meter in the soil surface reservoir	[$kg_s\ m^{-2}$]

The term A_s represents the imaginary amount of soil per square meter present in the soil surface reservoir. As in reality intake takes place from the first soil layer, A_s is calculated by multiplying the bulk density (ρ_b [$kg_s\ m^{-3}$]) of the upper soil layer with an imaginary thickness of the soil surface reservoir ($\Delta z(0)$ [m]). The thickness $\Delta z(0)$ can be calculated by relating it to the total amount present in the first soil layer.

$$A_s = \rho_b(1) * \Delta z(0)$$

and

$$\Delta z(0) = \Delta z(1) * \frac{(M_{sa}(1) + M_{sl}(1))}{M_{ss}}$$

where

$M_{sa}(1)$ = mass of chemical adsorbed in layer 1 [$kg_c\ m^{-2}$]
$M_{sl}(1)$ = mass of soluted chemical in layer 1 [$kg_c\ m^{-2}$]
$\Delta z(1)$ = thickness of layer 1 [m]

In order to omit difficulties in solving the differential equations the first order equation (5a) has been used. To do so A_s is calculated with the initial amount present at the soil surface.

$$\Delta z(0) = \Delta z(1) * \frac{(M_{sai}(1) + M_{sli}(1))}{M_{ssi}}$$

The subscribt $_i$ denotes the initial condition of a timestep.

The choice for intake from the soil reservoir is quite arbitrary. As a consequence intake by cattle is zero if M_{ss} is nil and the intake from the first soil layer is omitted. If in reverse intake is calculated from the first soil layer the strong gradient in dioxin content near the "soil surface" is neglected (unless a very small upper soil layer is discerned). From this it is clear that the division between soil surface and soil column is made for reason of modelling only (this distinction is very usefull in modelling the rainfall-dependent infiltration of soluble compounds; e.g. the application of fertilizer). It should be studied whether the intake by cows is simulated accurately in this way.

3.3 The soil-water subsystem

The soil-water subsystem is treated separately because of the specific character of the (transport)processes that act in this system. The soil-water subsystem is divided into the two elements soil surface and soil column. It is clear that the separation between those two elements is artificial and is made for reason of modelling. The soil surface is considered as a reservoir of deposited dioxins and furans where photodecomposition occurs and from where soluted compounds infiltrate into the soil column or will be consumed by the cattle. In the soil column physical transport processes dominate. In order to be able to calculate the distribution of water and soluted and adsorbed amounts of dioxin the soil column is divided into layers. Within each layer complete mixing is assumed. Removal of pollutants from these layers possibly occurs by plant uptake, biodegradation, leaching, drainage and volatilization. Because considerable differences in properties between the saturated and unsaturated zone (anaerobic and aerobic conditions respectively) occur in the soil-water system, the biological and chemical processes may differ for these two zones.

3.4 Processes of the soil-water subsystem

3.4.1 Infiltration

It has been assumed that the dioxins and furans enter the soil soluted into the water phase. This implies that the concentration of these polutants never can exceed the watersolubility. The rate of infiltration is calculated only if there is rainfall:

$$\left(\frac{dM}{dt}\right)_{inf} = P * C_p + \frac{M_{ssi}}{\Delta t} \qquad (6a)$$

If the average concentration exceeds the aqueous solubility, i is calculated by:

$$\left(\frac{dM}{dt}\right)_{inf} = P * S \qquad (6b)$$

with

$\left(\frac{dM}{dt}\right)_{inf}$	= infiltration rate	$[kg_c\ m^{-2}\ d^{-1}]$
P	= precipitation	$[m\ d^{-1}]$
C_p	= concentration in precipitation	$[kg_c\ m^{-3}]$
Δt	= length of timestep	[d]
S	= aqueous solubility	$[kg_c\ m^{-3}]$

3.4.2 Sorption

The lipophylic character of the PCDDs and PCDFs renders them very sensitive to adsorption to organic soil particles. Transport processes, dependent on the solution present, will be retarded or even prohibited. Although this is not conform to reality, in the model the sorption process is considered to be reversible, and equilibrium is assumed to be reached instantaneously. Two formulas that describe sorption are the Langmuir equation:

$$Q = \frac{M_m * b * C}{(1 + b * C)} \qquad (7a)$$

where

Q	= amount adsorbed per amount of adsorbent	$[kg_c\ kg_s^{-1}]$
C	= concentration in solution	$[kg_c\ m^{-3}]$
M_m	= amount adsorbed per amount of adsorbent forming a complete monolayer	$[kg_c\ kg_s^{-1}]$
b	= constant related to energy of sorption	[-]

and the Freundlich isotherm:

$$Q = k * C^{1/n} \qquad (7b)$$

where

k	= equilibrium constant	$[m_l^3\ kg_s^{-1}]$
n	= degree of nonlinearity	[-]

The Langmuir isotherm is based on the following assumptions:
- the energy of adsorption is constant and independent of the extent of the surface coverage,
- there is no transmigration between the adsorbed molecules
- the maximum adsorption equals an saturated monolayer of solute molecules on the adsorbent surface.

The Freundlich isotherm is an empirical model. For certain circumstances both equations can be reduced:
- In the Langmuir relation the denominator equals 1 if low concentrations are present in the soil solution and as a result the Langmuir equation becomes linear.
- The coefficient n in the Freundlich equation varies around 1 for most substances. If n equals 1 the Freundlich equation also reduces to a lineair relation.

The linear formulation of the sorption process reads:

$$Q = K_d * C \qquad (7c)$$

with

K_d	= $k_{oc} * f_{oc}$ = distributioncoefficient between the surface and the solution	$[m^3\ kg_s^{-1}]$
k_{oc}	= distributioncoefficient between organic carbon and the solution	$[m^3\ kg_{oc}^{-1}]$
f_{oc}	= fraction organic carbon	$[kg_{oc}\ kg_s^{-1}]$

The amount adsorbed expressed in kg chemical per kg soil (Q) can be converted to the amount adsorbed expressed in kg chemical per square meter by multiplying Q with the bulk density ρ_b $[kg_s\ m^{-3}]$ and the layer thickness Δz [m].

3.4.3 Convection

Dioxins and furans are assumed to be transported in solution by water. Convection by other solvents, soluted organic matter and particles is neglected. The transport processes are considered to be homogeneous.

After discretising the soil column into layers of a certain thickness the moisture fraction of each layer at the end of the timestep can be calculated from the water balance if the boundary conditions, i.e. the water fluxes, are known. The water balance reads:

$$\frac{d(\theta * \Delta z)}{dt} = q_i - q_o - S \qquad (8)$$

with

θ	= volumetric water content	$[m_l^3\ m_s^{-3}]$
Δz	= layer thickness	$[m_s]$
q_i	= incoming fluxes	$[m_l^3\ m_s^{-2}\ d^{-1}]$
q_o	= outgoing fluxes	$[m_l^3\ m_s^{-2}\ d^{-1}]$
S	= source/sink term	$[m_l^3\ m_s^{-2}\ d^{-1}]$

The source/sink term for water equals the transpiration fluxes for most cases. The average moisture content during a timestep can be calculated assuming a linear change with time. The solute is transported with the water but at the same moment formation and/or degradation processes may occur. The transport of water and solutes is calculated simultaneously by solving the combined transport/conservation equation (Paragraph 3.5).

3.4.4 Diffusion

Diffusion due to concentration or temperature gradients leads to a redistribution of dioxins and furans in the soil profile. The presence of soil organic matter strongly hampers diffusion. As in the Lickebaert area peaty soils prevail, the role of diffusion for the Lickebaert area has been investigated before modelling started. Volatilization, defined as the diffusion through the soil surface from the underlaying soil layer appeared to be negligible (Appendices 1 and 2) for the Lickebaert area. For the calculation of volatilization, the driving force (the concentration gradient), was taken at maximum by assuming the concentration above the soil surface to be zero. Diffusion from one layer to another can only be less than the volatilization, due to the smaller concentration gradients. The conclusion is that diffusion is of no importance for the Lickebaert area and that no redistribution of PCDDs and PCDFs due to this process is to be expected. Consequently diffusion has not been incorporated into the model.

3.4.5 Runoff

As soon as the rainfall flux exceeds the saturated conductivity, excess rainfall will flow horizontal over the soil surface to a drainage system. The amount of dioxins transported in this way is calculated by multiplying the runoff flux with the concentration of the water at the soil surface.

3.4.6 Leaching and drainage

Leaching, defined as the flux of the chemical through a certain plane in the soil profile (for instance the groundwatertable as a moving plane or a certain depth below the soil surface as a constant bottom boundary), is one of the parameters that have to be evaluated in determining the environmental risk of the proposed measures for the Lickebaert area. Leaching defined in this way equals the amount of pollution added to the groundwater. Drainage, i.e. the lateral fluxes to the field drains, trenches, ditches and the canals, have to be investigated for the same reason. Incorporating drainage into a one-dimensional model extends the model to a pseudo-two dimensional model. For both leaching and drainage the water fluxes have to be delivered by a waterquantity model. Leaching and drainage of the chemicals are calculated with the combined transport/conservation equation (Paragraph 3.5).

3.4.7 Non-homogeneous transport

Non-homogeneous transport processes highly determine the distribution of chemicals with a low mobility such as the PCDDs and PCDFs. Heterogeneous transport can be simulated in a simple way by the simulation of bypass flow. For compounds that are almost immobile bypass flow has to be considered only during deposition. To model this type of bypass flow the deposition at the soil surface has to be divided into an amount that is added instantaneously into the soil profile and an amount remaining at the soil surface:

$$D_{ss} = \beta * (1-\alpha) * D$$

and (9)

$$D_{by} = (1-\beta) * (1-\alpha) * D$$

where

β = factor dividing the deposition at the soil surface [-]
D_{by} = bypass deposition rate [$kg_c\ m^{-2}\ d^{-1}$]

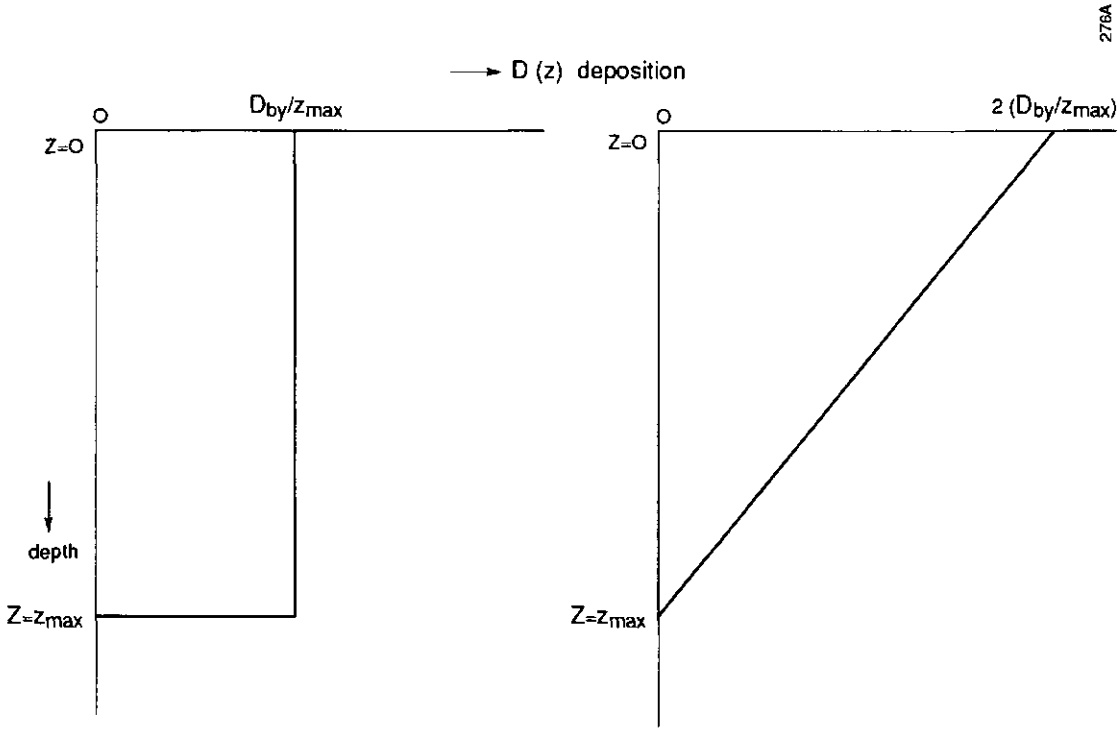


Figure 4 The non-homogeneous transport (bypass flow) functions.

The bypassed deposition has to be divided over the soil profile. There are two possibilities for $z < z_{max}$:

1) constant with depth;

$$D(z) = \frac{D_{by}}{Z_{max}} \quad (10a)$$

2) linear decreasing with depth;

$$D(z) = \frac{2 * D_{by}}{Z_{max}} * (Z_{max} - z) \qquad (10b)$$

Z_{max} is the maximum depth below soil surface where bypass flow occurs. A graphical presentation of the formulas 10 is given in Figure 4. For both approaches field data have to be available in order to identify the fitting function and the parameter β.

The amount deposition bypassed to the distinguished soil layers can be calculated by integrating over the depth. In each soil layer this amount has to be divided over the soluted and adsorbed phase.

3.4.8 Mixing processes

Mixing of the soil layers due to biological or mechanical activity is incorporated into the model. At pre-defined timesteps the amount of dioxins present in the soil layers (till a predefined depth) can be divided equally over these soil layers. This is done for both the amount adsorbed as well as for the amount in solution.

The formulation of the transport equation in the model in each soil layer assumes complete mixing within each soil layer. This mixing is called the numerical dispersion. The discretization in depth of the soil profile determines the magnitude of this numerical dispersion.

3.4.9 Biodegradation

Degradation processes in the soil moisture can be described by first order reactions (already described in Paragraph 3.2.3), but also by zero-order reactions:

$$\left(\frac{dM}{dt}\right)_{Bdg} = K_0 + K_f * \theta * \Delta z * C \qquad (11)$$

where

$\left(\frac{dM}{dt}\right)_{Bdg}$	= biodegradation rate	[$kg_c\ m^{-2}\ d^{-1}$]
k_0	= zero order degradation rate	[$kg_c\ m^{-2}\ d^{-1}$]
k_f	= first order degradation rate	[d^{-1}]

k_0 is calculated from the half-life by:

$$k_0 = \frac{M_0}{2 * t_{1/2}}$$

From available data the most suitable degradation reaction (first or zero order) has to be selected for application of the model.

3.5 The model

The elements of the soil-water-plant system and their relations as modelled are depicted in Figure 5.

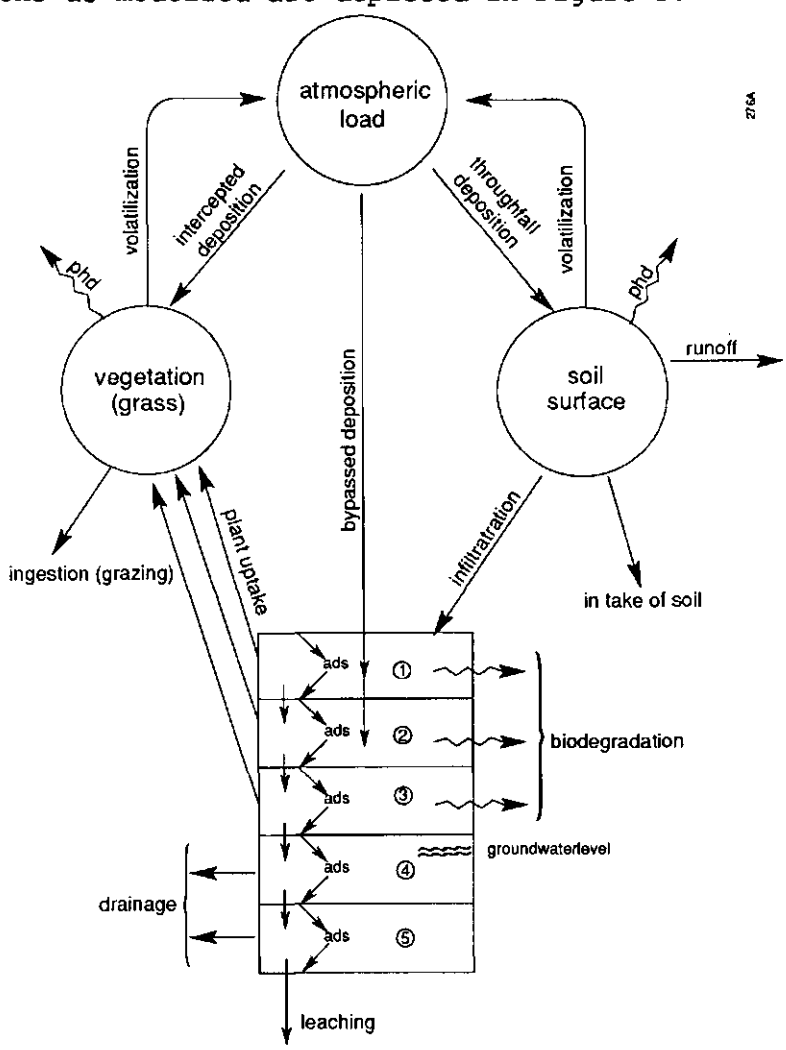


Figure 5 The fate of deposited PCDDs and PCDFs in the soil-water-plant model.

The (gross) deposition represents the total input of PCDDs and PCDFs into the system.

For each of the elements of the system (the vegetation, the soil surface and the soil column) the mass conservation equations can be made:

$$\frac{dM_v}{dt} = D_v + \left(\frac{dM}{dt}\right)_{Upt} - \left(\frac{dM_v}{dt}\right)_{Phd} - \left(\frac{dM}{dt}\right)_{Ing} \qquad (12a)$$

$$\frac{dM_{ss}}{dt} = D_{ss} - \left(\frac{dM_{ss}}{dt}\right)_{Phd} - \left(\frac{dM}{dt}\right)_{Inf} - \left(\frac{dM}{dt}\right)_{Int} \qquad (13a)$$

$$\frac{dM_s}{dt} = \frac{dM_{sl}}{dt} + \frac{dM_{sa}}{dt} \qquad (14a)$$

where:

$M_s = M_{sl} + M_{sa}$
= total amount of chemical present in the soil per square meter [$kg_c\ m^{-2}$]

$M_{sl} = \theta * \Delta z * C$
= amount of chemical present in the soil liquid per square meter [$kg_c\ m^{-2}$]

$M_{sa} = \rho_b * \Delta z * Q$
= amount of chemical adsorbed to the soil matrix per square meter [$kg_c\ m^{-2}$]

Considering convection by and degradation in the soil moisture only and inserting the equations 1 to 11 gives:

$$\frac{dM_v}{dt} = -k_1 * M_v + s_1 \qquad (12b)$$

$$\frac{dM_{ss}}{dt} = -k_2 * M_{ss} + s_2 \qquad (13b)$$

$$\frac{dC}{dt} = -k_3 * C + s_3 \qquad (14b)$$

with

$$s_1 = \alpha * D + q_t * C * r$$

$$s_2 = (1-\alpha) * \beta * D - P * C_p$$

$$s_3 = \frac{q_i * C_i + (1-\beta) * (1-\alpha) * D - kz}{(\theta * \Delta z * (1+kd))}$$

and

$$k_1 = \frac{k_v + nrc * I_v}{A_v}$$

$$k_2 = k_{ss} + \frac{(P * M_{ssi} + nrc * I_s * M_{ssi}/\Delta z(1))}{(M_{sai}(1) + M_{sli}(1)) * \rho_b(1)}$$

$$k_3 = \frac{q_o + q_t * r + k_f * \theta * \Delta z)}{(\theta * \Delta z * (1 + kd))}$$

The general analytical solution of these equations is:

$$M(t) = M_0 * e^{-k*\Delta t} + \frac{s}{k}(1 - e^{-k*\Delta t}) \qquad (15)$$

with

$M(t)$	= amount present at the end of the timestep (at time t)	$[kg_c\ m^{-2}]$
M_0	= amount present at time t_0	$[kg_c\ m^{-2}]$
Δt	= $t - t_0$ = timestep length	[d]

The solutions depend on the actual value of the variables. The solutions of equation 14 are treated extensively by Berghuijs-van Dijk et al. 1985. The water fluxes have to be delivered by a suitable waterquantity model. Equations 12 and 13 have to be solved for each timestep, equation 14 must be solved for each timestep and for each layer.

The averaged amount present during a timestep can be calculated by integrating over the timestep and dividing by the timestep. The general solution reads:

$$M_{av} = \left(\frac{1}{k * \Delta t}\right) * \left(M_0 - \frac{s}{k}\right) * (1 - e^{-k * \Delta t}) + \frac{s}{k} \qquad (16)$$

where

M_{av} = average amount present in a timestep $[kg_c\ m^{-2}]$

The averaged amount in a compartment of the model is used to identify the incoming amount into the next compartment (if there are waterfluxes from one compartment to the other).

3.5.1 The simplified model

The deposition data, calculated from the measured TCDD content of the soil, are the composite result of the actual deposition at the soil surface diminished with the dissipation processes (photodecomposition, ingestion, biodegradation, intake and volatilization) which occur after deposition. Therefore these data are net soil-deposition data and are not coherent with the required deposition input-data of the developed model. In order to perform the simulations with these net deposition data the model has to be simplified: all the dissipation processes have to be omitted. Under these circumstances the vegetation becomes an external element. The simplified model is given in Figure 6 and consists of only two elements; the soil surface and the soil column. As a matter of fact, this simplified system is equal to the soil-water subsystem (Paragraph 3.3 and 3.4) without sink processes.

The simplified model is fully described by the equations:

$$\frac{dM_{ss}}{dt} = D_{ssr} - \left(\frac{dM}{dt}\right)_{inf} \qquad (13c)$$

$$\frac{dM_s}{dt} = q_i * C_{in} - q_o * C \qquad (14c)$$

where D_{ssr} denotes the reduced (nett) deposition at the soil surface.

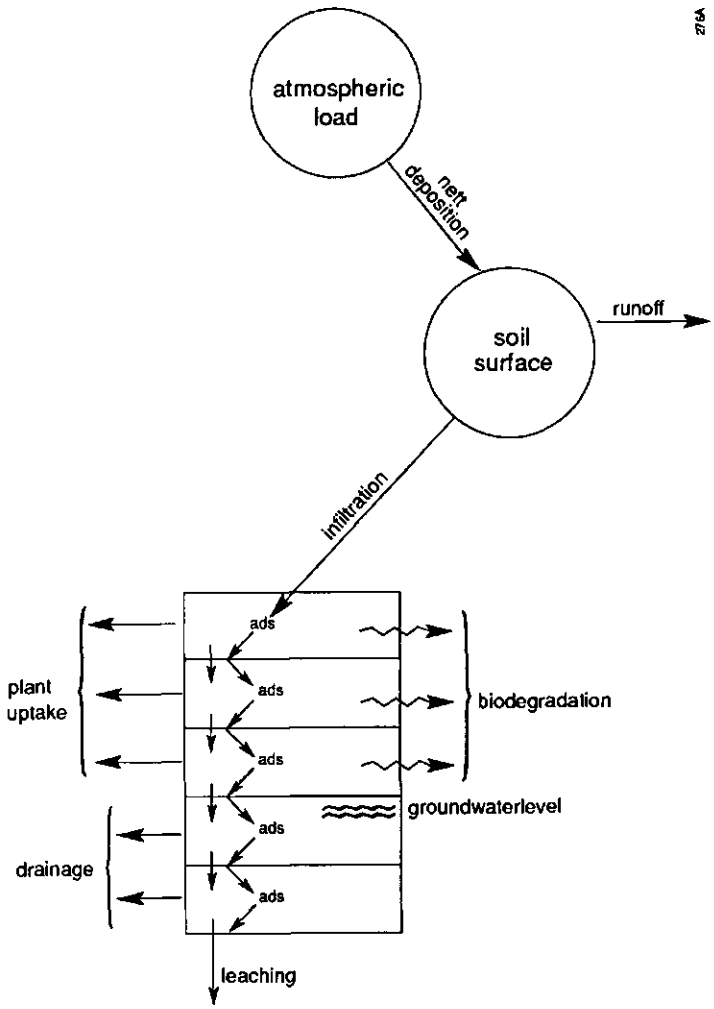


Figure 6 The fate of on the soil deposited PCDDs and PCDFs in the soil-water model.

3.5.2 Implementation of the model

The TRANSOL simulation model (Rijtema and Kroes 1990) based on the solutions of equation 14 as described by Berghuijs-van Dijk et al. (1985b), covers the soil-water system. This model served as the basis for the development of the FAD (FAte of Dioxins) model. The division of the soil-water system into the elements soil surface and soil column made it possible to maintain the body of TRANSOL unchanged. By adding or modifying some subroutines the preliminary FAD model has been realised. The FAD model has been developed to describe the fate of dioxins and furans in the soil-water-plant system. In general the FAD model can be used to study the fate of a single chemical in the environment for which gas phase transport is of minor importance (gas phase transport is not yet included into the model), which is soluble in water and which is subject to decomposition at the soil surface, at the vegetation and in the soil profile.

Compared to TRANSOL the subroutines SURF, PLANTS, INPDIO, OUTDIO and INIDIO have been changed or added. The subroutine SURF calculates per timestep the division of the deposited chemicals at the soil surface. The subroutine PLANTS calculates the presence of the deposited chemicals at the vegetation per timestep. A new common block containing the additional common variables has been introduced. The subroutine INIDIO determines the initial data for the calculations of the next timestep. For lack of suitable measured data the FAD model has not been validated and could not be applied to the Lickebaert area in order to evaluate the effects of the proposed technical interventions.

The equations of the simplified model are completely covered by TRANSOL (Rijtema and Kroes 1990).

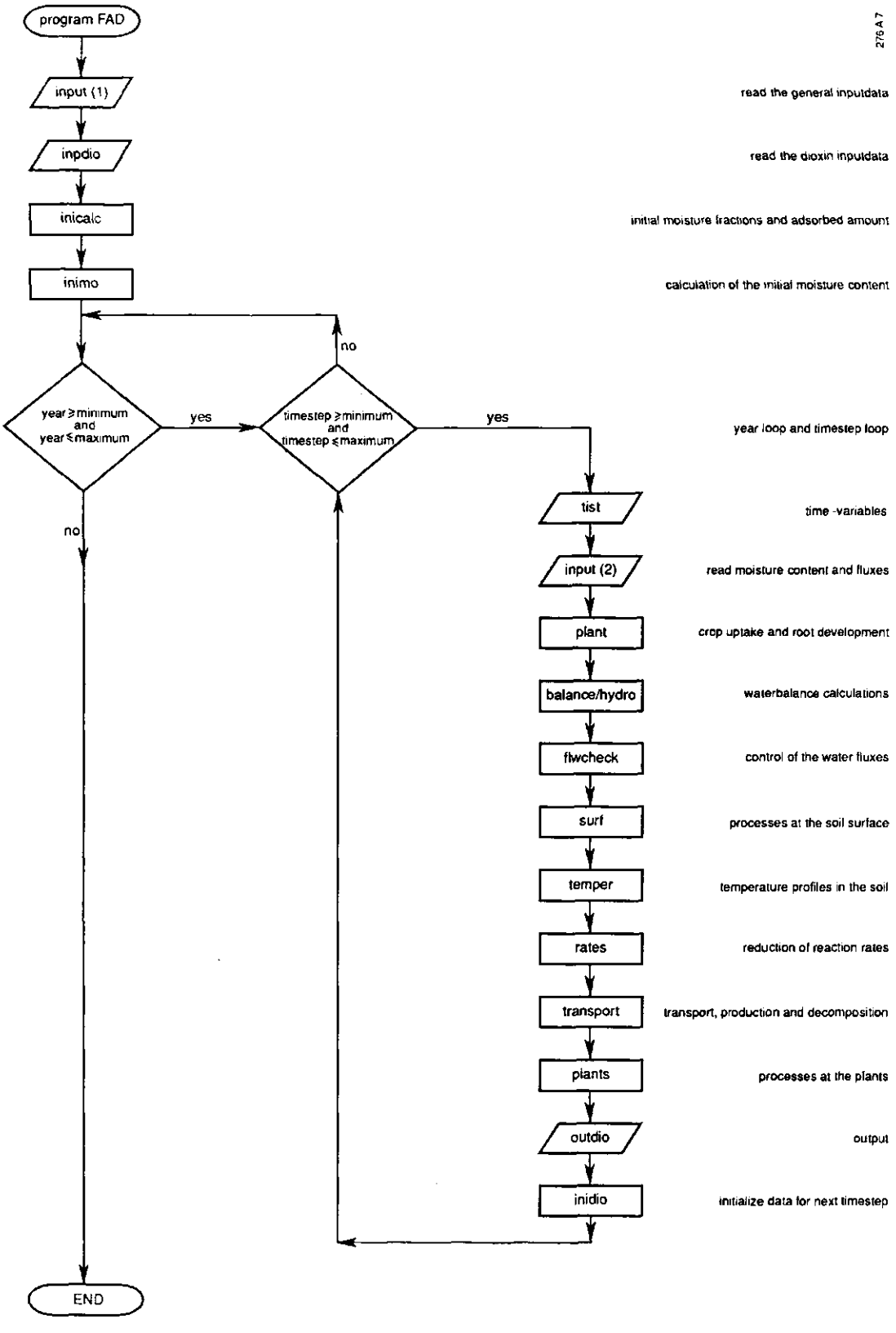


Figure 7 Flow chard of the program FAD.

4 APPLICATION OF THE SIMPLIFIED MODEL

4.1 Definition of the problem

The aim of this study was to evaluate the environmental effects of the proposed agricultural measures for the Lickebaert area. In order to rehabilitate the Lickebaert area for agricultural use the following technical interventions have been suggested:

1 Two-phase ploughing; the contaminated upper 10 cm of the soil profile will be transported to a depth of 30 cm below soil surface.
2 Mixing of at least the upper 30 cm of the soil profile with a frasing-machine.
3 Removing the polluted soil and store it in a safe dump-site.

These solutions were proposed assuming that the contamination of the cows was mainly caused by intake of soil while grazing. The aim of these measures therefore is to decrease the concentrations in the upper soil layer in order to reduce intake by cows. In the proposed interventions the source of release was not considered. The literature review led to doubt on the general assumption leading to this measures: that intake of soil would be the major path of contamination of the cattle. If the intake of grass is the main path, there must be a more or less continuous deposition because photodegradation seems to be rather fast. Therefore the effect of closure of the sources also has been investigated.

The environmental effects of the suggested measures have to be known. The following objectives should be met by measures to be taken:

- Dioxins should become almost immobile.
- There should be no uptake by plants or transport to the soil surface leading to re-contamination.
- No leaching or drainage of dioxins should take place unless degradation occurs under anaerobic circumstances or the polluted water is mixed with large amounts of uncontaminated water.

In order to investigate whether the effects of the measures agree with the environmental criteria, the displacement of dioxins has been simulated for four different scenarios during a thirty year period. The scenarios are:

1 The present situation as initial condition and a continuing emission.
2 The present situation as initial condition and sanitation of the source (no deposition).
3 Ploughing down the toplayer to a depth of 30 cm below soil surface as initial condition and a continuing emission.
4 Ploughing down the toplayer to a depth of 30 cm below soil surface as initial condition and sanitation of the source.
5 Mixing of the upper thirty centimeters of the soil profile and a continuing emission.
6 Mixing of the upper thirty centimeters of the soil profile and sanitation of the source.
7 To dig out the surface layer and store the soil material in a dump-site.

The last option results in an (almost) uncontaminated initial condition. If the emission continues, pollution will build up again. Because the resulting contamination is only dependent on the amount of deposition, this option has not been investigated.

4.2 Inputdata

The Lickebaert area (480 ha) is situated west of Rotterdam and north of the Nieuwe Waterweg between Vlaardingen and Maassluis. Clay soils and peat soils dominate this area. The land use is mainly agricultural, being grassland for milk-production. A map (1 : 25 000) of the soils in the Lickebaert area is presented by Boels et al. (1990). From these data a representive soil profile has been selected for which the proposed interventions are applicable from the agricultural point of view. The profile equals a 40 cm clay layer on a peaty subsoil. The required hydrological inputdata are obtained by use of the WATBAL waterbalance model (Berghuijs-van Dijk 1985a).

Data used for the simulation of the hydrogical situation in the Lickebaert area by the WATBAL model are:
- The meteorological data (precipitation and open water evaporation) are historical time series obtained from KNMI. Used are the data from De Bilt for the period from 1952 to 1981.
- Soil physical data from the Staring-series (Wösten et al. 1987) have been used. Unit B18 has been taken to represent the clay toplayer and unit O17 for the peaty basis. These profiles have been selected based on the soil-physical measurements (h-θ relations and K_{sat} values) sampled by the SC for the agricultural evaluation of the interventions in the Lickebaert area.
- The properties determining the drainage have been calibrated until the results fitted an averaged highest groundwaterlevel of 34 cm - ss and an averaged lowest groundwaterlevel of 74 cm - ss (groundwater-class IIb, classification from the soil map of the Netherlands).

Results from the WATBAL model are presented in Table 1. From the waterbalance it can be seen that most of the precipitation will evapotranspirate, that leakage is small, that drainage mainly occurs by the trenches and that the storage is large (due to the high saturated water content of the soil). This abstract schematization is assumed to be representative for the (average) hydrological situation in the Lickebaert area, although this is arbitrary.

The input-data used in the simulation with TRANSOL are:
- The waterfluxes between the soil layers are obtained from the WATBAL calculations.
- The present situation, the initial condition for evaluating the solutions proposed, is simulated by calculating a 30 year period with a constant concentration of the rainwater.

Table 1 Waterbalance for the soil layers 0 to 10 (terms in mm year^{-1}).

Balance period		Precipi-taton	Drainfluxes from			See-page	Evapo-transp.	Leakage	Drainflux to			Runoff	storage +=incr.	Balance deviation
			trench	ditch	canal				trench	ditch	canal			
0-1952/	0-1953	802.	0.	0.	0.	0.	483.	34.	0.	190.	10.	0.	85.	0.
0-1953/	0-1954	597.	0.	0.	0.	0.	525.	34.	0.	168.	9.	0.	-139.	0.
0-1954/	0-1955	818.	0.	0.	0.	0.	440.	34.	0.	196.	10.	0.	138.	0.
0-1955/	0-1956	663.	0.	0.	0.	0.	456.	34.	0.	210.	10.	0.	-47.	0.
0-1956/	0-1957	748.	0.	0.	0.	0.	460.	34.	0.	246.	10.	0.	-2.	0.
0-1957/	0-1958	928.	0.	0.	0.	0.	488.	35.	0.	353.	10.	0.	42.	0.
0-1958/	0-1959	828.	0.	0.	0.	0.	499.	35.	0.	307.	10.	0.	-23.	0.
0-1959/	0-1960	536.	0.	0.	0.	0.	380.	34.	0.	172.	9.	0.	-60.	0.
0-1960/	0-1961	929.	0.	0.	0.	0.	479.	34.	0.	276.	10.	0.	128.	0.
0-1961/	0-1962	925.	0.	0.	0.	0.	513.	35.	0.	368.	10.	0.	0.	0.
0-1962/	0-1963	750.	0.	0.	0.	0.	507.	34.	0.	292.	10.	0.	-93.	0.
0-1963/	0-1964	777.	0.	0.	0.	0.	491.	34.	0.	225.	10.	0.	17.	0.
0-1964/	0-1965	760.	0.	0.	0.	0.	516.	34.	0.	162.	9.	0.	39.	0.
0-1965/	0-1966	1152.	0.	0.	0.	0.	500.	35.	7.	508.	11.	0.	91.	0.
0-1966/	0-1967	1148.	0.	0.	0.	0.	492.	35.	9.	598.	12.	0.	2.	0.
0-1967/	0-1968	853.	0.	0.	0.	0.	472.	35.	3.	360.	10.	0.	-27.	0.
0-1968/	0-1969	858.	0.	0.	0.	0.	484.	35.	0.	426.	11.	0.	-98.	0.
0-1969/	0-1970	747.	0.	0.	0.	0.	496.	34.	0.	240.	10.	0.	-33.	0.
0-1970/	0-1971	908.	0.	0.	0.	0.	512.	35.	0.	305.	10.	0.	46.	0.
0-1971/	0-1972	562.	0.	0.	0.	0.	464.	34.	0.	163.	9.	0.	-109.	0.
0-1972/	0-1973	656.	0.	0.	0.	0.	497.	34.	0.	86.	9.	0.	30.	0.
0-1973/	0-1974	780.	0.	0.	0.	0.	502.	34.	0.	166.	10.	0.	68.	0.
0-1974/	0-1975	993.	0.	0.	0.	0.	531.	35.	0.	306.	10.	0.	112.	0.
0-1975/	0-1976	635.	0.	0.	0.	0.	468.	34.	1.	302.	10.	0.	-180.	0.
0-1976/	0-1977	536.	0.	0.	0.	0.	383.	34.	0.	100.	9.	0.	10.	0.
0-1977/	0-1978	813.	0.	0.	0.	0.	470.	34.	0.	221.	10.	0.	78.	0.
0-1978/	0-1979	644.	0.	0.	0.	0.	449.	34.	0.	195.	10.	0.	-45.	0.
0-1979/	0-1980	873.	0.	0.	0.	0.	481.	35.	0.	301.	10.	0.	46.	0.
0-1980/	0-1981	862.	0.	0.	0.	0.	479.	35.	0.	327.	10.	0.	11.	0.
0-1981/365	-1981	958.	0.	0.	0.	0.	543.	35.	0.	373.	10.	0.	-2.	0.

- The total deposition is estimated by RIVM at 50 till 70 ng teq m^{-2} $year^{-1}$ during a 25 year period and 20 ng teq m^{-2} $year^{-1}$ since about 1990 (Langeweg, 1990 personal communication). The factor α used to determine this amount equaled 0.8. In applying the simplified model it is supposed that the deposition of dioxins is only due to rainfall. The concentration of dioxin in the rainwater is calculated by dividing the yearly averaged deposition of TCDD (50 ng teq $year^{-1}$) by the yearly averaged amount of precipitation (0.8 m^3 m^{-2} $year^{-1}$). The calculated concentration of 2*10E-10 mol l^{-1} almost equals to the aqueous solubility of TCDD. For use in the calculations the concentration of dioxins in the rainwater is put at 62.5 ng m^{-3}.
- The soil physical parameters are given in Table 2:

Table 2 Soil physical parameters used in TRANSOL.

	Rootzone	Underground	
bottom boundary	40	100	[cm - ss]
dry bulkdensity	800	200	[kg m^{-3}]
organic matter fraction	.2	.85	[kg kg^{-1}]

- The sorption rate of dioxins to soil organic matter is selected to be 500 m^3 kg^{-1}, sorption is calculated linear. The value of 500 m^3 kg^{-1} equals the lowest K_{oc} value of TCDD resumed by Van der Bolt (1990). The lowest K_{oc} leads to the highest mobility thereby being the worst case for studying environmental effects.
- The factor determining the uptake by plants is set at 0, so plant uptake initially has been omitted.
- Biodegradation is omitted in the calculations as this process is very uncertain to occur. Therefore the degradation rate in the model is put at zero.
- Horizontal transport at the soil surface due to wind erosion has been neglected because of the high lutum content of the upper soil layer in the Lickebaert area.
- Non-homogeneous transport has not been taken into account as no field data on the importance of such processes in the Lickebaert area are available.
- Mixing due to biological processes between different soil layers has not been considered.

4.3 Calculated results of the simulation runs

Results of the simulation run for estimating the initial situation:
- The calculated amount deposited dioxins varies from 33 to 72 ng m^{-2} $year^{-1}$ due to the used series of meteorologic data.
- The calculated distribution of dioxin over the soil profile shows a strong dependence on the discretization of the soil column. This is caused by the assumption of complete mixing within each soil layer. The thickness of the soil layer thereby determines the overall effect of these processes in the calculations. Figure 8 indicates the calculated distribution of dioxin in the soil profile in dependence of the discretization of the soil profile.

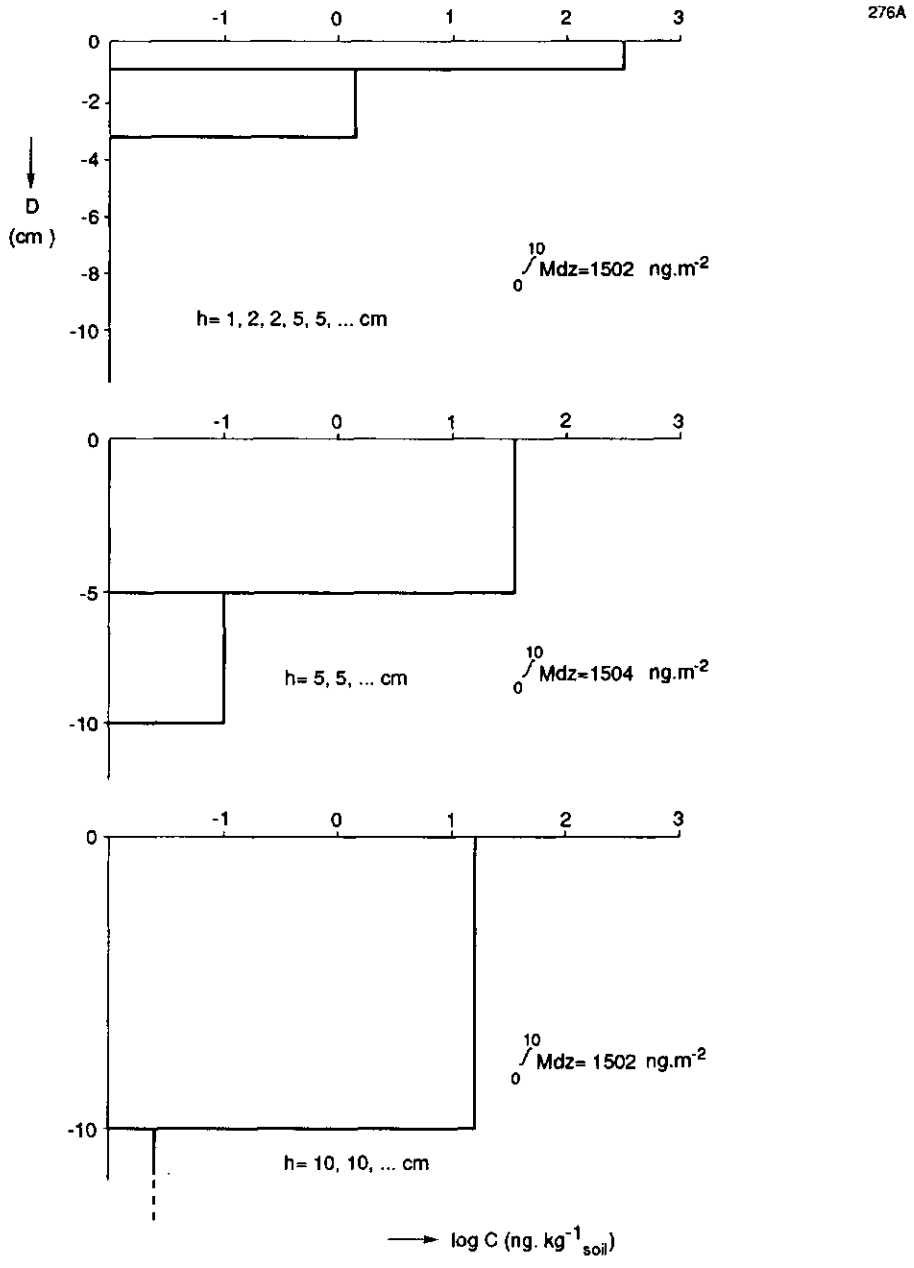


Figure 8 Distribution of dioxin in the soil profile as calculated with TRANSOL for thicknesses of < 5, 5 and 10 cm of the soil layers.

- The total amounts of dioxins present in the upper 10 cm of the soil profile is equal for the four calculated cases (as it should be because almost no dioxin is present below 10 cm - ss and because no degradation processes are taken into account).
- The steep gradient in the distribution for small layers is the effect of the strong adsorption of dioxins to organic matter.
- If the layer thickness is < 5 cm the calculated dioxin concentration for the upper 5 cm of the soil exceeds the measured concentrations due to the omission of photodegradation within this part of the soil. These

discretization thereby can not approximate the distributions measured by RIVM.
- A 10 cm layer thickness leads to a dioxin concentration of 19 ng kg^{-1} after thirty years (Fig. 8), which value is almost identical to the averaged value of the measurements over the first 10 cm of the soil in the Lickebaert area (18 ng teq kg^{-1}).
- Below this first 10 cm of soil the calculated concentrations of dioxin are negligibly small (Figure 8).
- The calculated concentration of dioxin in the soil moisture is far below the aqueous solubility.
- As expected, the model calculations show a strong adsorbtion of dioxins to the soil organic matter making the dioxins nearby immobile (Table 3).
- Removal of dioxins by drainage or leaching is almost absent for the selected hydrological schematization (Table 3).
- Runoff due to excess rainfall hardly occurs for the chozen hydrological schematization (Table 3).
- The calculated balance deviations presented in Table 3 are the results of the rounding off procedure used in TRANSOL.

Results of specific processes:
- Passive uptake of dioxins has been calculated in an additional simulation run and equalled 0.025 ng m^{-2} (transpiration flux of 477 mm $year^{-1}$) for the last year of the calculation on the initial period. This amount is about 1 promille of the amount adsorbed in that year. The final distribution in the soil profile was not influenced.
- The amounts of dioxins soluted in the soil moisture are negliglible as compared to the amount adsorbed to the soil organic matter.
- Global comparison of calculations on the initial situation and scenario 2 show dioxins to be almost immobile. The amount transported is about 0.1% of the amount initially present in the first soil layer. On the very long term this will result in a significant downward movement and in a redistribution of dioxins in the soil profile. This process is limited by irreversible adsorption and the rate of downward transport will decrease with decreasing dioxin content and therefore decreases in time. On the short term, say 100 years, the downward transport is less then 1% and seems negligibly.
- It can be seen from the initial situation and scenario 1 that the additional pollution gives rise to an increase in the amounts stored in the toplayer. The increase during this 30 year period is smaller than during the initial 30 year due to the reduced emission.
- Scenario 4 compared to scenario 2 shows an increased downward transport (because of the higher volumetric water content at this depth), being about 0.3% of the amount initially present in layer 4. Also upward transport has been calculated. This must be caused by upward fluxes due to capillary rise and upward seepage.
- The difference between the scenarios 3 and 4, the deposition, affects the layers 1 and 2 during the 30 year period. The amounts calculated for these layers in scenario 3 therefore equal the deposition during this period at an uncontaminated surface (scenario 7, Paragraph 4.1).

Table 3 Mass-balance of dioxin in the soil-water system (terms in ng m^{-2} $year^{-1}$) for calculation of the momentary situation.

Balance period		Addi-tions	Depos. wet	Infil-tration	See-page	Uptake	Decom-position	Leakage	Drai-nage	Run-off	Volati-lization	Storage (incr) solution	Storage (incr) adsobed	Balance deviation
0-1952/	0-1953	0.000	50.131	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.625	49.506	0.000
0-1953/	0-1954	0.000	37.337	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	37.337	0.000
0-1954/	0-1955	0.000	51.119	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	51.118	0.000
0-1955/	0-1956	0.000	41.438	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	41.438	0.000
0-1956/	0-1957	0.000	46.775	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	46.775	0.000
0-1957/	0-1958	0.000	57.981	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	57.980	0.000
0-1958/	0-1959	0.000	51.731	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	51.731	0.000
0-1959/	0-1960	0.000	33.488	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	33.486	0.001
0-1960/	0-1961	0.000	58.044	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	58.043	0.000
0-1961/	0-1962	0.000	57.838	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	57.837	0.000
0-1962/	0-1963	0.000	46.869	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	46.867	0.001
0-1963/	0-1964	0.000	48.544	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	48.543	0.001
0-1964/	0-1965	0.000	47.506	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	47.506	0.000
0-1965/	0-1966	0.000	71.994	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.002	71.992	0.000
0-1966/	0-1967	0.000	71.750	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	71.748	0.001
0-1967/	0-1968	0.000	53.319	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	-0.002	53.320	0.000
0-1968/	0-1969	0.000	53.594	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	53.594	0.000
0-1969/	0-1970	0.000	46.669	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	46.670	-0.001
0-1970/	0-1971	0.000	56.781	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	56.781	0.000
0-1971/	0-1972	0.000	35.113	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	35.109	0.003
0-1972/	0-1973	0.000	41.025	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	41.023	0.001
0-1973/	0-1974	0.000	48.737	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	48.738	-0.001
0-1974/	0-1975	0.000	62.044	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.001	62.043	-0.001
0-1975/	0-1976	0.000	39.687	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	-0.001	39.688	0.001
0-1976/	0-1977	0.000	33.519	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	33.520	-0.001
0-1977/	0-1978	0.000	50.812	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	50.813	0.000
0-1978/	0-1979	0.000	40.225	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	40.227	-0.002
0-1979/	0-1980	0.000	54.569	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	54.566	0.002
0-1980/	0-1981	0.000	53.863	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	53.863	-0.001
0-1981/365-1981		0.000	59.900	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	59.902	-0.003

Results of calculations on the intervetions proposed are shown in Table 4.

Table 4 Calculated adsorbed amount of dioxin [ng teq/kgsoil] for each soil layer in the initial situation and for four scenarios:

Layer number	Depth (m - ss)	Initial	Scenario 1	2	3	4
1	.0- .1	18.7	24.9	18.7	6.21	0.
2	.1- .2	0.024	0.046	0.040	0.007	0.
3	.2- .3	0.	0.	0.	0.002	0.002
4	.3- .4	0.	0.	0.	18.7	18.7
5	.4- .5	0.	0.	0.	0.081	0.081
6	.5- .6	0.	0.	0.	0.	0.
7	.6- .7	0.	0.	0.	0.	0.
8	.7- .8	0.	0.	0.	0.	0.
9	.8- .9	0.	0.	0.	0.	0.
10	.9-1.0	0.	0.	0.	0.	0.

Scenario's:
1 The present situation as initial condition and a continuing emission.
2 The present situation as initial condition and sanitation of the source (no deposition).
3 Ploughing down the toplayer to a depth of 30 cm below soil surface as initial condition and a continuing emission.
4 Ploughing down the toplayer to a depth of 30 cm below soil surface as initial condition and sanitation of the source.

- The same distribution is obtained by substracting the results of scenario 1 and 2. The scenarios 5 and 6 have been calculated by assuming linear behaviour (caused by the strong adsorption). Scenario 6 then leads to a distribution of 6.24 ng teq/kgsoil for the first three soil layers and no dioxin in the lower layers, whereas scenario 5 shows a distribution of 12.45, 6.25, and 6.24 for the layers one to three and no dioxins below layer three.
- Scenario 3 and 7 are the most effective of the proposed interventions in order to reduce the dioxin content of the upper soil layer.
- Sanitation of the source is necessary if recontamination should be prevented.
- As there exist no limits for maximum allowed dioxin contamination in the Netherlands, none of the proposed measures can be rejected at this moment. Research should be done to determine such a limit.
- None of the solutions is in conflict with the environmental criteria that have been defined (Paragraph 4.1).

4.4 Conclusions

Since some process-parameters are not known and as results of the measurements from the Lickebaert area are lacking the simulation results have to be interpreted very carefully. The simulated impact of the involved processes should be considered as an intelligent, but rough estimate of reality, and provides insight in the importance of these processes under certain conditions.
The following conclusions have been drawn from the application of the simplified model to the Lickebaert area on the processes:

- Dioxins in the Lickebaert area hardly move in the water-soil system due to the high organic matter content of the soil. This also holds true after transportation of the polluted top layer to greater depths by ploughing.
- For the same reason passive uptake by plants is neglectable for the Lickebaert area.
- The concentrations of dioxins into the drainagewater and the groundwater did not exceed the chemically detection limit for these chemicals. Transport of dioxins to the groundwater or the open water is highly unlikely for the selected hydrological schematization and omitting non-homogeneous transport.
- It is not possible to obtain the measured distribution of dioxins in the soil profile by using the simplified model if photodegradation is not taken into account. Simulation of photodegradation is not possible as long as no accurate deposition data become available.

This leads to the evaluation of the interventions:
- All measures proposed to decontaminate the polluted soil are suitable from the environmental point of view.
- Soil contamination will increase or will start again as long as the emission of dioxins continues.

Finally some general remarks have to be made:
- The short time period available and the lack of available data made it neccesary to simplify the modelled system. Consequently the results are of limited validity and should be interpreted very carefully.
- Because of the limited validity of the quantitative data the qualitative results from the literature review (Van der Bolt 1990) should be used in addition in order to evaluate the measures suggested.
- In order to provide better results the model has to be extended and tested. This requires more time and more data. This concerns not only monitoring data from pollution in the environment, but also additional data on processes. Detailed laboratory and field experiments in order to understand the processes, to collect processparameters and to prepare datasets for validation of the model, are required.

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Appendix 1 Derivation of a diffusion equation in order to estimate the volatilization flux of dioxins through the soil surface.

To derive an equation that describes the volatilization through the soil surface by diffusion from the underlying soil three equations are used as starting point;

Ficks first law:

$$\frac{dq_g}{dt} = - D * \frac{dC_g}{dx} \qquad (1)$$

with

q	= flux per unit area	[mol m^{-2}]
t	= time	[d]
D	= diffusivity	[m^2 d^{-1}]
C	= concentration	[mol m^{-3}]
x	= distance	[m]
$_g$	= denoting the gas phase	

Henrys law:

$$P_g = H * C_l \qquad (2)$$

where

P_g	= partial gas pressure	[N m^{-2}]
H	= Henry's constant	[Nm mol^{-1}]
$_l$	= denoting the liquid phase	

and the general gas law:

$$P_g * V_g = n * R * T \qquad (3a)$$

Rearranging equation 3a, assuming a constant temperature gives:

$$\Delta P_g = \Delta\left(\frac{n}{V_g}\right) * R * T$$

$$= \Delta\, C_g * R * T \qquad (3b)$$

Combining equation 3b with equation 1 and taking the boundary condition $P_{atm} = 0$ for x = 0 (the soil surface) and assuming the pressure in the soil to be constant gives:

$$\frac{dq_g}{dt} = \frac{D}{x} * \frac{P_{gsoil}}{R * T}$$

as an expression for the volatilization flux over a certain soil layer from depth x to the soil surface (depth is zero). Inserting equation 2 into 4:

$$\frac{dq_g}{dt} = - \frac{D}{x} * \frac{H * C_1}{R * T} \qquad (5)$$

C is a function of the amount adsorbed:

$$C_1 = \frac{q_{ads}}{L * \rho_b * K_{om} * M_{om}} \qquad (6)$$

with:

q_{ads}	= amount adsorbed	[mol m^{-2}]
L	= thickness of soil layer	[m]
ρ_b	= dry bulk density	[kg_s m^{-3}]
K_{om}	= partition coefficient between water and organic matter	[m^3 kg_{om}^{-1}]
M_{om}	= weight fraction org. matter	[kg_{om} kg_s^{-1}]

Introducing corrections for structure of the soil and the moisture content of the soil and relating the concentration in the soil moisture to the amount sorbed (eg. 6) equation 5 is expanded to:

$$\frac{dq_q}{dt} = - \tau * \Phi_g * \frac{D}{x} * \frac{H}{R * T} * \frac{q_{ads}}{L * \rho_b * K_{om} * M_{om}} \qquad (7)$$

with

τ	= tortuosity	[-]
Φ_g	= $\theta_{sat} - \theta_{act}$ = air filled pore volume	[-]

Assuming the volatilization flux equal to the change in the adsorbed amount of dioxins, i.e. $dq_g = dq_{ads}$; which seems reasonable for compounds with a low water solubility and a large k_{oc}, and introducing:

$$\mu = \frac{D * H * \tau * \Phi_g}{R * T * \rho_b * K_{om} * M_{om}}$$

and:

$x = \beta * L$
with $\beta = \{1, 2, 3, \ldots\}$

leads to

$$\frac{dq_{ads}}{dt} = - \frac{\mu}{\beta L^2} * q_{ads} \qquad (7a)$$

integration over time yields:

$$q_{ads}\ (t) = q_{ads}\ (t=0) * e^{\left(\frac{-\mu}{\beta L^2} * \Delta t\right)} \qquad (8)$$

The volatilization rate can be estimated by:

$$\frac{dq_g}{dt} = \frac{q_{ads}\ (t) - q_{ads}\ (t=0)}{\Delta t} \qquad (9)$$

$$= q_{ads}\ (t=0) * e^{\left(\frac{-\mu}{\beta L^2} * \Delta t\right)}$$

and the first order half-life is approximated by:

$$t_{1/2} = Ln(2) * \frac{\beta L^2}{\mu} \qquad (10)$$

Appendix 2 Application of the steady state diffusion equation to the Lickebaert area.

To estimate the influence of volatilization on the dissipation of dioxins and furans in the Lickebaert area representive data have to be used in the formulas derived in Appendix 1.

The data for the worst case approximation are:
1 General data:

$R = 8{,}3144$ Nm mol^{-1}
$T = 273 + 12 = 285$ K
(12°C equals the yearly averaged soil temperature in the Netherlands)
$\tau = 1$ (worst case)
$\Phi_g = \theta_{saturated} = 0.72$ (worst case)
$D = (0.1, \ldots, 10) * 10^{-11}$ m^2 s^{-1} (estimated)
$H = 1, \ldots, 10$ (Shiu et al., 1988)

2 Specific data for the Lichebeart area:

$\rho_b = 800$ kg m^{-3}
$M_{om} = 0.2$ kg_{om} kg_s^{-1}
$K_{om} = 500$ M^3 kg^{-3}

Inserting these data in formulas (for derivation see Appendix 1)

$$\frac{dq_g}{dt} = q_{ads}\,(t=0) * e^{\left(\frac{-\mu}{\beta L^2} * \Delta t\right)}$$

and

$$t_{1/2} = \mathrm{Ln}\,(2) * \frac{\beta L^2}{\mu}$$

with:

$\Delta t = 1$ year
$\beta = 2$
$q_{ads}(t=0) = 20$ ng T_{eg}/kg_s^{-1} in the upper 1 cm soil ($L = 0.01$ m)

and:

$\mu = 1.52 * (E\text{-}17, \ldots, E\text{-}20)$

gives for the Lickebaert area:

$$\frac{dq_g}{dt} \approx q_{ads}(t=0) * (1-1) = 0$$

and

$t_{1/2} = 9.1 * (E+12, \ldots, E+15)$ year.

Indicating that volatilization of dioxins from the upper 0.005 m of soil (β * L) is expected to be very small and of no importance if other dissipation processes, like photodegration, occur at the same moment ($t_{1/2}$ (photodegration) < 1 year).