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Dutch Risk Assessment System for New Chemicals: Soil-Groundwater Module

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ABSTRACT

A new Soil-Groundwater Module has been developed for incorporation in the Dutch Risk Assessment System for New Chemicals. In this module, the accumulation in the uppermost soil layer one year after sewage sludge application and the maximal concentration in the deeper groundwater of new substances due to sewage sludge application are determined as criteria for the exposure of humans and the environment to these substances. For each new xenobiotic substance and specific-substance dose rate both criteria can be quantified by interpolation for the specific sorption coefficient based on organic matter, K_{om}, and the half-life, DT_{50}-soil, of this substance and multiplication by the actual substance dose rate (kg/ha). Therefore, the K_{om} and DT_{50}-soil should be determined from the n-octanol/water distribution coefficient, K_{ow}, and the Readily Biodegradability test result, respectively.

The calculation procedure is incorporated in the menu driven computer program of the Risk Assessment System.

SAMENVATTING

Ten gevolge van toepassing van zuiveringsslib kunnen nieuwe xenobiotische stoffen in het bodem-grondwatersysteem komen.
Een nieuwe Bodem-Grondwater Module is ontwikkeld, welke ingebouwd wordt in het Beoordelingssysteem voor Nieuwe Chemische Stoffen. In het betreffende module worden de volgende criteria gehanteerd voor de mate van blootstelling van mens en milieu aan deze nieuwe xenobiotische stoffen:

- de accumulatie in de bovengrond, één jaar na toediening van de zuiveringsslib;
- de maximale concentratie van het diepere grondwater.

De geaccumuleerde hoeveelheid in de bovengrond kan expliciet worden berekend met behulp van het model PESTLA. Dit model is ontwikkeld ten behoeve van de berekening van de uitspoeling van bestrijdingsmiddelen en wordt in Nederland gebruikt in het kader van de toelating van bestrijdingsmiddelen.

Met het doel de concentratie van het diepere grondwater te bepalen wordt in een eerste stap de uitspoeling en daarmee de concentratie van het *bovenste* grondwater met behulp van het model PESTLA berekend. In een tweede stap wordt het transport van het bovenste grondwater naar het *diepere* grondwater beschouwd, gebaseerd op een eenvoudig analytisch principe. Als een worst-case benadering worden zowel sorptie en omzetting, als diffusie en dispersie in de verzadigde zone verwaarloosd. Dientengevolge resulteert de concentratie van het diepere grondwater uit de concentratie van het bovenste grondwater en de areaalfractie (het met zuiveringsslib belaste gedeelte van een intrekgebied).

Door middel van interpolatie voor de stofspecifieke op organische stof gebaseerde sorptiecoëfficiënt, K_{om} en de half-waardetijd, DT_{50}-soil, en vermenigvuldiging met de actuele hoeveelheid stof (kg/ha) is met behulp van het Bodem-Grondwater Module de actuele accumulatie en maximale concentratie van het diepere grondwater te berekenen voor een specifieke stof en stof-belasting. Voor deze berekening dienen de K_{om} en DT_{50}-soil te worden bepaald uit de n-octanol/water-verdelingscoëfficiënt, K_{ow}, respectievelijk het Readily-Biodegradability-toetsingsresultaat.

Met betrekking tot de concentratie van het diepere grondwater is een inschatting te maken voor de *worst-case* situatie.

Tevens is het mogelijk een indicatie te verkrijgen van

- de *actuele* gehaltes van de bovengrond één jaar na de toediening van zuiveringsslib (accumulatie);
- de *actuele* maximale concentratie van het *bovenste* grondwater.

Tenslotte kan een ruwe indicatie worden verkregen van de concentratie van het *diepere* grondwater.

De berekeningsprocedure is ingebouwd in het menugestuurde computerprogramma van het Beoordelingssysteem. Voor toepassing van het programma zijn slechts de K_{om} en de Dt_{50} als input parameters benodigd.

SUMMARY

New xenobiotic substances may be introduced in the soil-groundwater system by sewage sludge application to the soil.
To determine exposure of human and the environment to these substances, a new Soil-Groundwater Module has been developed that will be incorporated in the Dutch Risk Assessment System for New Chemicals. The exposure of humans and the environment to these new xenobiotic substances is determined on the basis of the following criteria, determined in this module:

- the accumulation in the uppermost soil layer one year after sewage sludge application;
- the maximal concentration in the deeper groundwater.

The accumulation of the substance in the topsoil layer can be explicitly calculated using the PESTLA model.

In order to determine the maximal concentration in the deeper groundwater, the first step concerns the determination of the maximal concentration in the *uppermost* groundwater using the PESTLA model. In a second step, the migration of substances, based on a simple analytical approach, from the uppermost groundwater to the *deeper* groundwater is considered. As a worst-case approach, sorption and transformation as well as diffusion and dispersion are neglected in the saturated zone. As a consequence, the maximal concentration in the deeper groundwater is assumed to be a function of the maximal concentration in the uppermost groundwater and areal fraction only, the areal fraction being the fraction of the groundwater capture zone under sewage sludge application.

In the Soil-Groundwater Module the actual accumulation and maximal concentration in the deeper groundwater for a specific substance and specific-substance dose rate can be determined by interpolation for the specific sorption coefficient based on organic matter, K_{om}, and half-life, DT_{50}-soil, of this substance and by multiplication by the actual dose rate (kg/ha). Therefore, the K_{om} and DT_{50}-soil should be determined from the n-octanol/water distribution coefficient K_{ow} and the Readily Biodegradability testing result, respectively.

For the *worst-case* approach a prediction can be made for the maximal concentration in the deeper groundwater. Furthermore, it is possible to indicate

- the *actual* contents in the uppermost soil one year after sewage sludge application (accumulation) and
- the *actual* maximal concentration in the *uppermost* groundwater.

A rough estimation can be made for the *actual* maximal concentration in the *deeper* groundwater.

The calculation procedure is incorporated in the menu driven computer program of the Risk Assessment System. When applying the program, the K_{om} and the DT_{50} are the only input parameters needed.

1. INTRODUCTION

1.1 General context

Since 1987 the policy reflected in the 'Kennisgevingsbesluit Wet Milieugevaarlijke Stoffen' (Code on legislation for environmentally hazardous substances) has been followed in the Netherlands. In this policy, admission criteria for new chemical xenobiotic substances (new substances) have been defined. With the purpose of quantifying the risk for humans and the environment due to the exposure to new substances the 'Dutch Risk Assessment System for New Chemicals' (DRANC), has been developed by the Dutch National Institute of Public Health and Environmental Protection (RIVM).

In the DRANC calculation modules representing separate environmental compartments, as shown schematically in Figure 1, have been interconnected. Each module quantifies emission, migration and/or effects of substances for the respective environmental compartments. For a more detailed description of the DRANC the reader is referred to *Van der Poel (1991)* and *Toet et al. (1991).*

Within the framework of the development of the DRANC a new module concerned with the soil-groundwater compartment is described in this report. The module includes the quantification of:

- the accumulation of a substance in the topsoil layer one year after sewage sludge application and
- the maximal concentration in the deeper groundwater

due to the use of sewage sludge applied on agricultural land and/or grassland. The pathways that are the subject of the Soil-Groundwater Module under investigation in this report are represented by heavy lines in Figure 1.

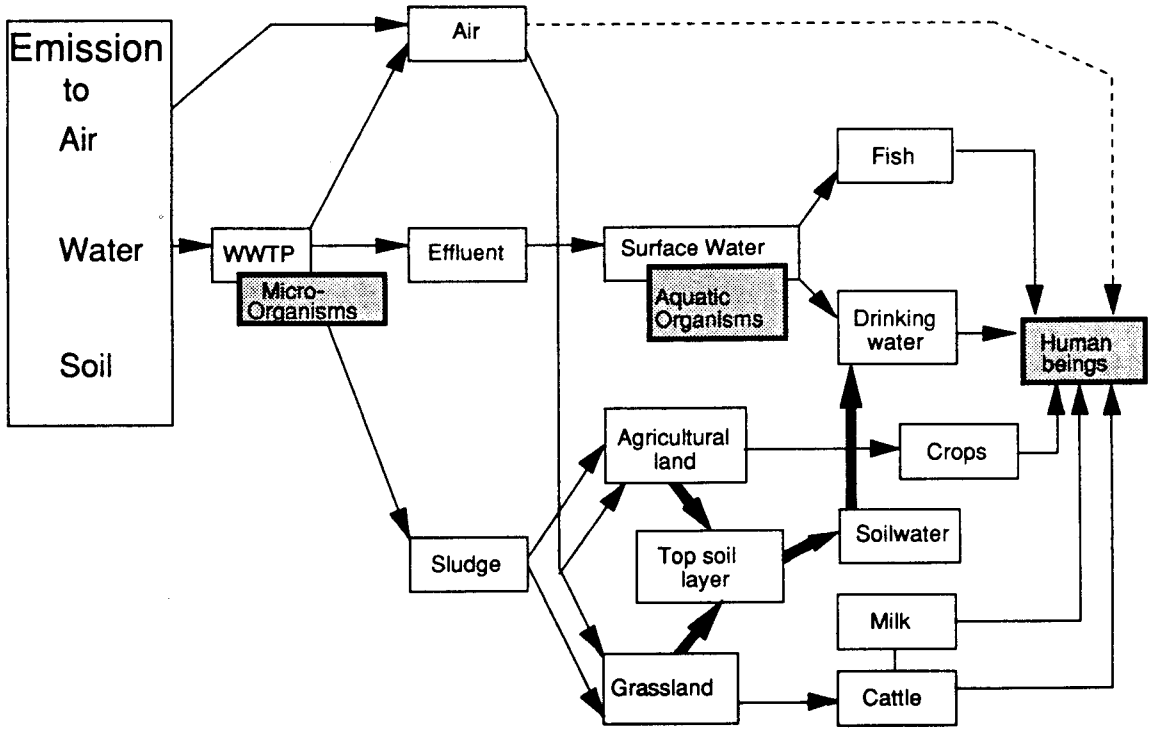

Figure 1: Schematic presentation of the calculation modules and their interaction in the Dutch Risk Assessment System for New Chemicals. The heavy lines represent the Soil-Groundwater Module under investigation in this report.

As new xenobiotic substances generally concern organic chemicals, attention in this study is focused on organic substances. However, in principle, the same procedure is valid for *inorganic* xenobiotic substances.

The Soil-Groundwater Module has recently been incorporated in the USES (Uniform System for Evaluation of Substances) prototype II (*Ministerie van Volkshuisvesting, Ruimtelijke Ordening en Milieubeheer et al. 1992*).

1.2 Pre-requisites for the Risk Assessment System

The use of the DRANC is based on the following pre-requisites (*Toet et al. 1991*):

- meant for use in the Netherlands;
- exposure assessment not site specific but based on a 'standard environment',

which can be classified as relatively vulnerable (worst-case approach);
- emissions regarded as point sources;
- environmental risk based on the PEC/NEC ratio (PEC = Predicted Environmental Concentration; NEC = No Effect Concentration).

Concerning environmental implications for soil and groundwater, there is much similarity between organic new substances and pesticides. However, the range for the main input parameters considered for assessment of environmental implications of new substances is larger than usual for pesticides. For practical reasons, the same procedure will be followed for new substances as for pesticides, where the range for these input parameters has been increased.

1.3 Outline

Chapter 2 will outline the processes that determine leaching and accumulation. Further, the numerical model, PESTLA, used to quantify accumulation and leaching, and the required input parameters will be described.
The definition for accumulation is given in Chapter 3, where also the procedure for quantifying accumulation in the topsoil layer will be described.

The water quality of the aquifers (deeper groundwater) is assessed using two steps:

- in the first step, the maximal concentration in the *uppermost* groundwater is calculated with the PESTLA model (Chapter 4);
- in the second step, the maximal concentration in the *deeper* groundwater is calculated taking the maximal concentration in the uppermost groundwater as starting-point (Chapter 5).

The substance dose rate on the soil and time of substance load are handled in Chapter 6.
Chapter 7 describes the procedure of the Soil-Groundwater Module and the results of the calculations. The accuracy of the Soil-Groundwater Module is the subject of discussion in

Chapter 8.
Finally, conclusions from the study have been drawn up and recommendations for further research are presented in Chapter 9.

Appendix 1 lists definitions and symbols in alphabetical order.
In Appendix 2 the table shows calculated accumulation and maximal concentration in the deeper groundwater, as the basis for the Soil-Groundwater Module in the Dutch Risk Assessment System for New Chemicals.

2. LEACHING AND ACCUMULATION

Both leaching and accumulation are determined by migration and behaviour of the substance in the soil. The PESTLA model *(Van der Linden and Boesten, 1989)*, based on the one-dimensional convection/dispersion transport equation for reacting and degradable solutes in soil, performs simultaneous calculation of migration and behaviour. This model has been developed for the evaluation of pesticide leaching from the upper soil into the water-saturated zone. It is used for supporting the decisions on admission of pesticides in the Netherlands (*Ministerie van Landbouw, Natuurbeheer en Visserij, 1991*).

2.1 Processes in the PESTLA model

The following processes can play a role of importance in describing the migration of organic solutes in soil:

- Transport processes:
  - convection: solute movement along with the moving water mass;
  - diffusion: solute movement within the water phase due to a concentration gradient; aims at minimal free energy;
  - dispersion: solute movement caused by inhomogeneous soil structural features.
- Sorption:
  - physical/chemical interaction between substances in the soil liquid and solid phases; for organic solutes, chemical forces are considered dominant for sorption.
- Transformation:

  Irreversible conversion of a substance due to (micro)biological processes and/or abiotic processes (hydrolysis, photodegradation).
- Soil-plant interaction:

  Uptake of soil water and substance from the soil by the plant roots.

Transport

Water flow has been based on the Darcy equation, while a fixed groundwater level at a depth of 1 m is assumed. Therefore, the soil hydraulic functions (i.e. the water content and unsaturated hydraulic conductivity) have to be defined as a function of pressure head. Diffusion and dispersion have been described by the well-known Fick equation (*Cussler, 1984*).

Sorption

Sorption results in a reduction of the velocity of the solute migration. As a further consequence of sorption, total transformation of the substance increases because more time is available for transformation before the substance is washed out. Moreover, total transformation also increases when the substance is retarded, because transformation is usually more intensive at lower depths, where bioactivity is known to be higher. Sorption has been described by an exponential relationship between substance in the solid and the liquid phases, i.e. the Freundlich sorption isotherm:

$$c_s = K_f \cdot c_l^{\,1/n} \qquad (1)$$

c_l = concentration in liquid phase [M L^{-3}]
c_s = concentration in solid phase [M M^{-1}]
K_f = Freundlich sorption coefficient [L^3 M^{-1}]
1/n = Freundlich exponent [-]

Because sorption is assumed to take place on soil organic matter the K_f is a function of the K_{om} [M L^{-3}], the sorption coefficient based on organic matter, and the fraction organic matter, f_{om} [-]:

$$K_f = K_{om} \times f_{om} \quad (2)$$

As the average of a wide range of pesticides, 1/n has been taken as 0.9 (*Van der Linden and Boesten, 1989).*

Transformation

The transformation rate in the soil is taken as a pseudo first-order equation, where the transformation rate is a function of the *total* concentration in the soil:

$$R_{tr} = k \times c_{tot} \quad (3)$$

where

R_{tr} = transformation rate [M L^{-3} T^{-1}]
k = transformation rate coefficient in soil [T^{-1}]
c_{tot} = total concentration substance [M L^{-3}]

Note that transformation is calculated as function of the total amount of substance, in the liquid as well as in the solid soil phase (expressed as substance mass per volume of wet soil). This procedure is in agreement with experimental determination, where transformation rate is determined in fresh soil samples from the field.

The transformation rate in soil is represented by the half-life, DT_{50}-soil [T], being the time in which half the substance mass in soil has disappeared. The relation between the rate coefficient, k, and the DT_{50}-soil is:

$$k = \frac{\ln 2}{DT_{50}\text{-soil}} \qquad (4)$$

Root uptake

Water uptake by roots has been described as a function of potential evapotranspiration, root depth and soil moisture. Substance uptake by roots is assumed to be passive and is a function of water uptake and substance concentration. Uptake of water and substance by plants results in a decrease of the substance content on a larger time scale.

2.2 Calculation of leaching and accumulation

The migration of substances in soil can be quantified by a combined description of the processes mentioned in Section 2.1. The resulting overall equation is known in the literature as the convection-dispersion equation, which name unfortunately does not account for the rather complex physical/chemical and microbiological processes like sorption and transformation. With this equation the concentration in the liquid phase, c_l, and the content of the solid phase, c_s, can be calculated explicitly at any given time and depth. For a more detailed evaluation of the description of the separate processes and calculation procedures, a review in *Bear and Verruijt (1987)* is recommended.

In the PESTLA model the convection-dispersion equation is solved numerically. Because the model has been developed for the evaluation of pesticides a pulse type single-dose application at the upper boundary, as is common in pesticide practice, has been included in the model. This type of application is comparable with sewage sludge application.

Another type of input, for example a daily dose due to atmospheric deposition, could, if appropriate for the expert system, be incorporated in the module as well.

2.3 Input parameters

The main input parameters, required to simulate substance migration from the soil surface to the uppermost groundwater with the PESTLA model, are:

- sorption coefficient based on organic matter, K_{om}, representing the sorption characteristics of the substance in soil;
- half-life, DT_{50}-soil, representing the transformation rate of the substance in soil;
- the substance dose rate entering the soil through the soil surface.

Furthermore, data should be available on:

- meteorological characteristics as a function of time (e.g. daily rainfall, potential evaporation);
- soil physical/chemical characteristics (soil bulk density, organic matter content);
- soil hydraulic characteristics and
- development of above-ground and underground vegetation.

It has been proven that model calculations are especially sensitive to uncertainty in the sorption coefficient, K_{om}, and transformation parameter, DT_{50}-soil (*Boesten, 1991*). These parameters can be assessed from the information legally required for new substances:

- the n-octanol/water distribution coefficient, K_{ow} (see Section 2.4);
- the Readily Biodegradability test result (see Section 2.5).

2.4 Determination of the sorption coefficient, K_{om}

A test to determine the n-octanol/water distribution coefficient, K_{ow}, [-] is prescribed for new substances. However, as an input parameter for the PESTLA model the sorption coefficient based on organic matter, K_{om}, is required. This parameter can be derived with the help of the following empirical relation (*Karickhoff, 1981*):

$$K_{oc} = 0.411 \times K_{ow} \qquad (5)$$

where K_{oc} = sorption coefficient based on organic carbon [L^3 M^{-1}].

Taking 0.5 for the ratio f_{oc}/f_{om} (*Scheffer and Schachtschabel, 1989*), we can derive:

$$K_{oc} = 2.0 \times K_{om} \tag{6}$$

where f_{oc} = fraction organic carbon [-].

Combining Eqns. 5 and 6 yields:

$$K_{om} = 0.2 \times K_{ow} \tag{7}$$

2.5 Determination of the half-life, DT_{50} soil

Determining the transformation rate in soil is not legally required. However, the transformation rate for a substance in soil can be derived from the Readily Biodegradability (RB) test result, which is legally required for each new substance. However, the RB test is performed in water and the result thus has to be translated into transformation data valid for the three-phase soil system.

2.5.1 Readily Biodegradability test

According to the OECD (Organisation for Economic Cooperation and Development) the Readily Biodegradability (RB) test can be classified as a 'category I test' (*OECD, 1979; OECD, 1990*). The result of such a test only distinguishes between 'readily biodegradable' and 'not readily biodegradable'; it does not quantify the transformation rate (note that

transformation = degradation). In the OECD procedure, a substance is defined as readily biodegradable if it is degraded completely 'within a short period', in the case of an application dose which is not extremely high. Characteristic for the RB test is that the substance is the only carbon source for the microorganisms and the biomass is relatively small. For quantifying the degradation rate a non-specific analytical procedure should be applied.

Several types of RB tests are registered. For the purpose of standardizing the experimental procedure, RB tests should meet the following conditions:

- A test period of 28 days.
- At the beginning of the experiment a possible lag period in which no transformation occurs, caused by time needed for the microorganisms to adapt to the substance. Biodegradation is assumed to have started as when 5% degradation is observed.
- The criterium for RB: under aerobic conditions, the substance should be largely transformed (i.e. 50-70%, depending on the specific RB test) within a period of 10 days. The amount of transformed substance is determined by measuring either the CO_2 production, BOD (Biochemical Oxygen Demand) or DOC (Dissolved Organic Carbon).

Besides the category I tests the following tests are also described by the OECD:

- Category II tests. Objective: to examine if a substance is able to transform ('potential transformation').

- Category III tests. Objective: to quantify the transformation rate.

Tests from categories II and III are not required and thus not standard procedures for new substances.

2.5.2 Transformation rate in water

The criterium for RB as mentioned above implies a maximal value of 0.5 x 10 days = 5 days for the half-life in water in the RB-test, DT_{50}-$water_{RB}$.

If a substance is not found to be readily biodegradable, but some degradation is observed within 28 days, the DT_{50}-$water_{RB}$ can be derived by an extrapolation procedure, as shown in Figure 2.

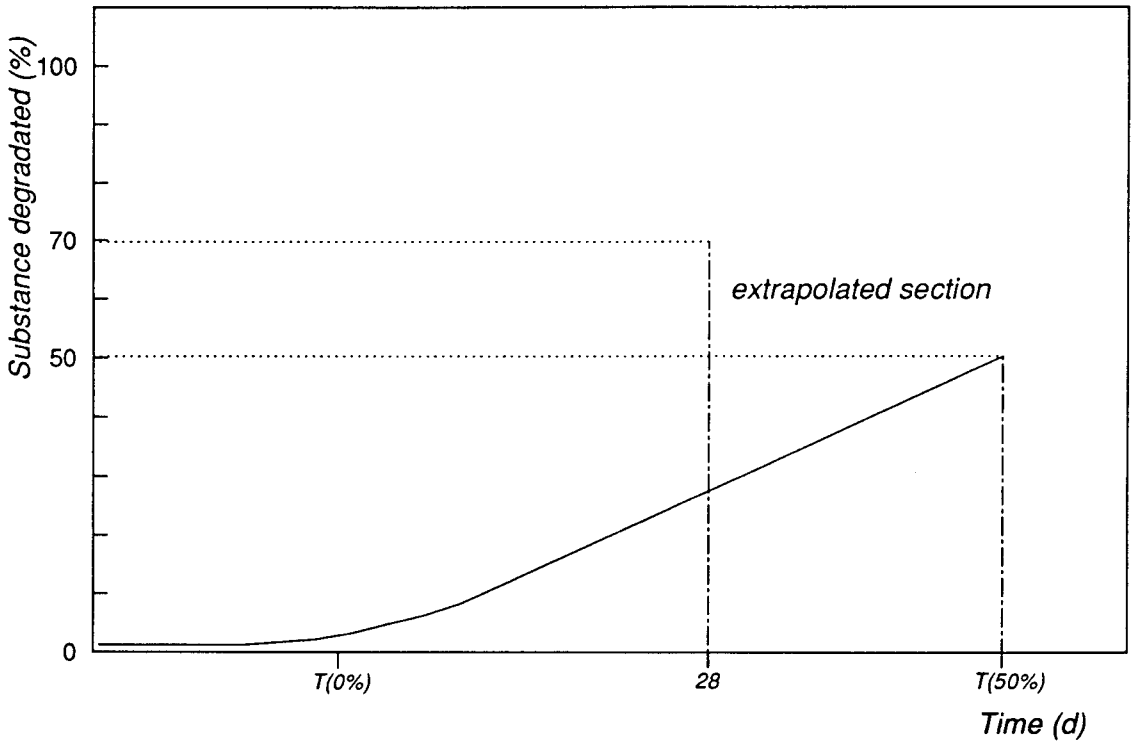

Figure 2: Example of degradation kinetics for graphical determination of the DT_{50}-$water_{RB}$ when the substance is not readily biodegradable; extrapolated DT_{50}-$water_{RB}$ = T(50%) - T(0%).

Figure 2 shows that for the substance in this example less than 70% has been degraded after a period of 28 days. For this reason, the degradation curve is linearly extrapolated until reaching the 50% degradation level ('extrapolated section'). The DT_{50}-$water_{RB}$ is than

determined simply by subtracting the lag period, T(0%), i.e. the period until 5% of the substance has been degraded, from the time the 50% degradation level has been reached, T(50%).

If no significant degradation has been observed within the period of 28 days, the substance is assumed to be persistent. DT_{50}-$water_{RB}$ is taken as maximal, i.e. 500 d. No significant degradation is defined here as less than 10% of the substance has been degraded, which means that no accurate extrapolation can be performed.

2.5.3 Transformation rate in soil

If the substance is readily biodegradable the DT_{50}-soil is taken as 5 d. If no significant degradation has been observed in the RB test for 28 days, DT_{50}-soil is taken as 500 d. If the substance is not readily biodegradable but more than 10% of the substance has been degraded in water within 28 days, the DT_{50}-soil has to be derived from the extrapolated DT_{50}-$water_{RB}$.

Differences in DT_{50}-values in both media are due to differences in biomass and availability of the substance. The latter is influenced in soil by a sorbing solid phase.

Correction for biomass

The representative biomass in the RB tests is about 3×10^4 - 30×10^4 CFU/ml (*Water Research Centre, 1981*). Population density in soil pore water is in the range of 2×10^6 to 200×10^6 CFU/ml, with the range 3×10^6 - 30×10^6 CFU/ml being representative (*Struijs and Van den Berg, 1992*). Under the assumptions that

- transformation is proportional to the population density and
- all micro-organisms reside exclusively in the pore water of the soil

it follows that the half-life is 100 times lower in the soil water than in the water of the RB test:

$$DT_{50}\text{-soil water} = 0.01 \times DT_{50}\text{-water}_{RB} \quad (8)$$

Note that this conversion is rather controversial from a microbiological point of view, because transformation is dependent on microbiological activity and species as well.

Correction for availability

Transformation has been assumed to take place in the soil water only, which implies that due to sorption a part of the substance in soil is not available for transformation. As a consequence, the DT_{50}-soil can be substantially higher than the DT_{50}-$water_{RB}$. The influence of sorption can be expressed with the help of the distribution coefficient, K_d [L^3 M^{-1}], which represents the mass ratio between a substance in the solid and liquid phases (simplification of the exponential Freundlich relation, Eqn. 1):

$$c_s = K_d \times c_l \quad (9)$$

Pseudo first-order transformation in the soil water, as a function of the concentration in the soil water, c_l, can be described as follows:

$$\frac{\partial c_l}{\partial t} = - k_{soil\ water} \times c_l \quad (10)$$

where t = time [T] and

$k_{soil\ water}$ = pseudo first-order transformation rate coefficient, *in the soil water phase* [T^{-1}].

To assess the pseudo first-order transformation rate coefficient *in the (total) soil*, k_{soil} [T^{-1}], Eqn. 10 must be written in terms of c_{tot} [$M\ L^{-3}$].

The relation between the substance in the liquid phase and the total soil content, c_{tot}, can be described with the help of the mass balance equation:

$$c_{tot} = \theta \times c_l + \rho \times c_s, \tag{11}$$

where ρ = density soil solid phase [M L^{-3}]

θ = volumetric water content [L^3 L^{-3}].

Note that the dimensions have different specifications for each medium:

c_{tot} [M L^{-3}_{soil}]

c_l [M $L^{-3}_{soil\ water}$]

c_s [M $L^{-3}_{solid\ phase}$].

From Eqns. 9 and 11 it follows that:

$$c_l = \frac{c_{tot}}{(\theta + \rho x\ K_d)} \tag{12}$$

Because no transformation takes place in the solid phase one may state:

$$\frac{\partial c_{tot}}{\partial t} = \frac{\partial(\theta\ c_l + \rho\ c_s)}{\partial t} = \theta\ \frac{\partial c_l}{\partial t} \tag{13}$$

$$\Leftrightarrow \frac{\partial c_l}{\partial t} = \frac{1}{\theta}\ \frac{\partial c_{tot}}{\partial t}, \tag{14}$$

if θ is considered as an average and constant (!) water content.

Substituting Eqns. 12 and 14 in Eqn. 10 yields:

$$\frac{\partial c_{tot}}{\partial t} = - \frac{\theta}{(\theta + \rho \times K_d)} \times k_{soil\ water} \times c_{tot} = - k_{soil} \times c_{tot} \qquad (15)$$

From Eqn. 15 it can be concluded that the pseudo first-order rate coefficients for transformation in soil and soil water are related as follows:

$$k_{soil} = \frac{\theta}{(\theta + \rho \times K_d)} \; k_{soil\ water} \qquad (16)$$

Because DT_{50} is inversely proportional to k, the half-lifetime in soil can be written as follows:

$$DT_{50}\text{-soil} = \frac{(\theta + \rho \times K_d)}{\theta} \times DT_{50}\text{-soil water} \qquad (17)$$

DT_{50}-soil

Taking into account the overall effect of the differences in biomass and the effect of the concentration ratio in soil and soil water on the magnitude of the DT_{50}-soil, the following relationship can be derived from Eqns. 8 and 17:

$$DT_{50}\text{-soil} = 0.01 \times \frac{(\theta + \rho \times K_d)}{\theta} \; DT_{50}\text{-water}_{RB} \qquad (18)$$

For the volumetric water content, θ, of a sandy soil 0.25 m^3/m^3 can be taken as an average

value over the year (corresponding with a pressure head of about $-10^{2.5}$ cm water, i.e. pF = 2.5). For the bulk density of the soil solid phase of a sandy soil a value of 1.4 $kg_{solid\ phase}/l_{soil}$ is representative. The distribution coefficient K_d can be approached by multiplication of the sorption coefficient based on organic matter, K_{om}, and the mass fraction organic matter for the upper layer of the Dutch standard soil (0.047): $K_d = 0.047 \times K_{om}$.

As a consequence, Eqn. 18 can be written as:

$$DT_{50}\text{-soil} = (0.01 + 0.0026 \times K_{om}) \times DT_{50}\text{-water}_{RB}, \qquad (19)$$

if c_l and c_s are expressed in $M/l_{soil\ water}$, $M/kg_{solid\ phase}$, respectively so that K_{om} is expressed in $l_{soil\ water}/kg_{soil}$.

According to this derivation of the DT_{50}-soil from the DT_{50}-$water_{RB}$ the influence of differences in system characteristics between soil and water have not been taken into account. These differences include:

- a higher aerobic micro biological activity in the soil due to a more intensive gas (oxygen) circulation;
- a possible catalizing effect of solid soil particles on transformation;
- a higher aerobic micro biological activity in soil due to the occurrence of organic matter;
- pH differences influencing transformation and hydrolysis.

3. ACCUMULATION IN THE TOPSOIL

In this study, accumulation is defined as the percentage of the amount of the substance applied, along with the sewage sludge left in the topsoil layer, after a period of one year. High accumulation of a xenobiotic substance could have a negative impact on the environment and/or human health.

Danger for the environment can result from:

- a direct threat through toxicological effects on plants, animals (including cattle) and soil (micro)organisms;
- an indirect threat due to a source of contamination for the groundwater and from other contaminants due to a reduction of the buffer capacity of the soil.

The same division holds for threats to human health:

- a direct threat due to human exposure to the contaminant (ingestion, dermal contact);
- an indirect threat through consumption of fruit and/or vegetables.

In the latter case, an increased amount of the substance can result from repeated consumption in the foodchain.

A high accumulation risk is expected for substances with a high half-life, DT_{50}-soil, *and* a high sorption coefficient, K_{om}. There is a low accumulation risk when the DT_{50}-soil *or* the K_{om} is low. For every other combination of DT_{50}-soil and K_{om}, the risk can hardly be predicted without calculation methods. For these substances the risk should be assessed with the help of the PESTLA model.

3.1 Calculation procedure

As mentioned in Section 2.2, the depth distribution of the contents in the solid and liquid soil phase results from the model simulations as a function of time. Accumulation in the topsoil layer, for example in the plough layer, can be calculated with the model by depth

integration of the total (solid *and* liquid phase) soil contents. In accordance with pesticide application, the substance is assumed to be distributed over a depth range of 5 cm in the initial state, i.e. directly after application time.

4. MAXIMAL CONCENTRATION IN THE UPPER GROUNDWATER

Leaching of a xenobiotic substance could imply a danger to the environment and/or human health. Due to the dominating effect of exposing human beings via drinking water, attention is focused on the quality of the deeper groundwater, used for drinking water preparation.

A high leaching risk is expected for substances with a high half-life, DT_{50}-soil, *and* a low sorption coefficient, K_{om}. There is a low leaching risk when there is a low DT_{50}-soil *or* a high K_{om}, at least on a relatively short time scale. For every other combination of DT_{50}-soil and K_{om}, the risk can hardly be predicted without calculation methods. For these substances the risk can be assessed with the help of the PESTLA model.

4.1 Drinking water

Drinking-water supply in the Netherlands (data 1988: VEWIN) is based on drinking water originating from groundwater (803 x 10^6 m^3/a ≈ 2/3) and from surface water (397 x 10^6 m^3/year ≈ 1/3).

Two factors, the soil profile and the aquifer characteristics, are of importance in relation to the vulnerability of the drinking-water reservoirs to leaching: the soil profile characteristics and the type of aquifer.

Soil profile

Sorption increases and vulnerability for leaching decreases with higher organic matter content. This study has considered a rather vulnerable soil type with respect to leaching: a sandy soil with moderately high organic matter content in the upper soil layer (4.7%) and a low organic matter content in the other soil horizons (0.8-0.1%). The sorption

characteristics of this soil type, which is rather common for a major part of the Netherlands, are relatively poor.

Aquifer

Phreatic aquifers are aquifers which are not protected by an overlaying clay layer and are in hydrostatic equilibrium with the atmosphere. Because of the lack of the protecting layer, phreatic groundwater is known to be the most vulnerable to groundwater contamination. However, the influence of the protecting layer is of minor importance for organic substances, for which leaching is more influenced by the organic matter content than by soil texture.

Pollution of a phreatic aquifer is considered in the Soil-Groundwater Module (worst-case approach). The relatively vulnerable areas with phreatic aquifers are situated mainly in the central and eastern part of the Netherlands. According to the VEWIN-statistics (1984) groundwater abstraction from phreatic and semi-confined aquifers is about a third of the total amount of groundwater abstraction. The contribution from the phreatic aquifers is only about 20% in the Netherlands.

4.2 Calculation procedure

As mentioned in Section 2.2, the depth distribution of the contents in the solid and liquid soil phases results from the model simulations as a function of time. In this study, the quality of the groundwater is related to the prevailing maximal concentration in the upper groundwater (at a depth of 1-2 m) during a leaching cycle, $c_{u,max}$. Calculation stops when less than 0.001% of the substance is left in the first metre of the soil profile, where disappearance can be caused by either leaching or transformation or a combination of these processes. In cases where more than 0.001 % of the substance is left after ten years and no maximal concentration in the uppermost groundwater has been reached within a period of ten years, leaching is not considered. For these substances, which possess a high

sorption affinity and/or a low transformation rate, the accumulation risk will be larger than the risk of leaching.

5. MAXIMAL CONCENTRATION IN THE DEEPER GROUNDWATER

After the substance has leached from the soil surface via the unsaturated zone into the uppermost groundwater, further downwards migration takes place to the aquifers (deeper groundwater), where groundwater abstraction for the preparation of drinking water occurs. Several processes could influence the water quality during this period. Because of the rather long migration distances no numerical models are used to calculate the water quality of the deeper groundwater. Instead, a rather simple analytical approach has been used.

5.1 Chemical/ biological processes

Analogous to the unsaturated zone, sorption of the substances in the *saturated* zone would result in a delayed substance migration velocity. As a consequence, transformation of the substance would increase due to higher residence times. However, although the role of sorption in the saturated zone still is matter of discussion, this process is assumed to be of minor importance due to the low organic matter contents in the aquifers. This assumption has been confirmed experimentally for some pesticides (*Van den Berg et al., 1990*). For this reason, sorption in the saturated zone is not taken into account in this study. Note that this conforms to a worst-case approach.

Also, not many research results on the role of transformation processes in the saturated zone have been reported (*Van den Berg et al., 1992*). Due to the small amount of biomass in the saturated zone and the prevailing conditions, no indications have been reported of this process being of significant importance for a wide range of pesticides (*Van de Weerd and Van der Linden, 1991*). However, *Van Beelen (1990)* showed that transformation in the saturated zone can occur for various organic contaminants. Because the role of transformation in the saturated zone is rather uncertain, the transformation in this zone is not taken into account in this study (worst-case approach).

New insights into both sorption and transformation in the saturated zone could lead to

adjustments in the Soil-Groundwater Module of the expert system in the future.

The residence time of the substance is, in relation to the influence of transformation in the saturated zone, even at a very small transformation rate, of overall importance. The time needed from entrance into the saturated water zone until arrival at the drinking water abstraction point depends primarily on the depth of groundwater abstraction. Furthermore, the local geohydrological situation influences the migration pattern and velocity, and thus residence time. In general, residence times can vary from a couple of years for the very shallow abstraction wells (at a depth of 10-20 m) to several decades or centuries for the deepest abstraction wells (*Mühlschlegel, 1989*). Note that even for one groundwater abstraction well, there is a fairly large distribution in residence times for substance particles entering the soil in the same period.

5.2 Hydraulic processes

Dilution of the groundwater can occur due to the following hydraulic processes:

- Mixture:

  The source of the three-dimensional pattern of flow lines, which meet in one groundwater abstraction well, can be traced back to the infiltration of (substance-loaded) water over a certain area. This area, in which the water particles enter the soil reaching the abstraction well within a certain time period (for example, 25 years), is known as the groundwater capture zone. Within the capture zone a part of the infiltrating water is of polluted origin, i.e. infiltrated on soil with sewage sludge application, while another part of the water is clean. As a consequence, the abstracted groundwater is bound to be a mixture of polluted and clean groundwater. The quality of this abstracted groundwater can be calculated if ideal mixing of the two types of water is assumed. For that reason, the fraction of polluted water, determined by the areal fraction, f_i [-], has to be assessed for a capture zone.

- Base flow:

  Groundwater transport in the saturated zone is characterized by a dominant horizontal water-flow component, with a huge spatial variation in the Netherlands (*Meinardi, 1991*). Also, an important depth variation in the base flow is found.
  In this study the influence of the base flow has not been considered, because exposure should not relate to a specific location. For the Netherlands as a whole, neglecting of the base flow comprises a worst-case approach for mixing the polluted groundwater with groundwater of a better quality.

- Vertical-smearing substance front:

  In the case of a single-substance application, e.g. when applying sewage sludge, the substance front will be prolonged vertically during transport due to diffusion and dispersion. As a consequence, the depth range of the substance front increases and the peak value (maximal content of the substance in the profile at a given moment) declines during transport. However, due to the non-linearity of these processes, no simple formula can be derived to include the smearing of the front due to dispersion and diffusion. In this study, vertical smearing due to diffusion and dispersion has not been taken into account (worst-case approach).

5.3 Estimation of the maximal concentration in the deeper groundwater

Analogous to the upper groundwater, attention has been focused on the *maximal* concentration in the deeper groundwater, $c_{d,max}$ [M L^{-3}].

Based on the assumptions discussed in Section 5.1 chemical-biological processes do not contribute to a concentration decrease during transport from the uppermost to the deeper groundwater. However, due to hydraulic processes (Section 5.2) a dilution of the polluted groundwater can occur. In this procedure only the mixing of the several water masses bound to infiltrate in the same groundwater capture zone has been taken into account. The maximal concentration in the deeper groundwater) can thus be calculated as follows:

$$c_{d,max} = c_{u,max} * f_i \quad (20)$$

where f_i = areal fraction [-].

6. SUBSTANCE LOAD

6.1 Sewage-sludge application

In the DRANC it has been assumed that the new substance enters the soil (through the soil surface) due to application of sewage sludge (see Figure 1). Sewage sludge should be applied to the soil surface as homogeneously as possible. So, the way that the substance enters the soil is analogous to the application of pesticides. No distinction is made between application to agricultural land or grassland.

Criteria for the composition of sewage sludge are based on the heavy metal content of the sludge. As a consequence, the amount of the organic substance under investigation is not the restricting factor for the admission of the sludge. Application of sewage sludge to non-agricultural soils is not allowed according to Art. 23 and 26 of the 'Besluit kwaliteit en gebruik overige meststoffen' (Code on quality and use of other fertilizers). Furthermore, sewage sludge should not be applied on snow- covered soils (Art. 28).

6.2 Areal fraction, fi

Two approaches are possible for the determination of the areal fraction:

- average approach, where the sewage sludge is assumed to be homogeneously distributed over agricultural areas → areal fraction = area of groundwater capture zones on agricultural land/total area of groundwater capture zones = 0.65 (data 1990: Wageningen Agricultural University, Department of Spatial Planning);
- worst-case approach, where the sewage sludge is assumed to be distributed over the whole area within the Groundwater Protection Area = area with sewage-sludge application → areal fraction = 1.

For the areal fraction the worst-case approach will be considered in this study (f_i = 1).

This implies that mixing of water masses of different quality has not been considered.

6.3 Substance dose rate

The time-dependent substance dose rate entering the soil through the soil surface varies because of different sewage sludge application doses and different amounts of the substance in the sludge. In the DRANC, the amount and quality of the sewage sludge are calculated in the Sludge Module (see Figure 1). Pathways from the Sludge Module are interconnected to agricultural land and grassland, as shown in the same figure.
Accumulation and maximal concentration in the deeper groundwater have been calculated for a substance dose rate of 1 kg/ha because:

- this amount is within the expected range of the amount of substance due to sewage-sludge application;
- this is a familiar amount for the application of pesticides.

Neither leaching nor accumulation respond linearly to the dose applied to the soil surface. This is due to non-linear sorption (i.e. the Freundlich sorption exponent, 1/n, = 0.9; see Eqn. 1).

As a first approach, maximal concentration in the deeper groundwater is assumed to respond linearly to the applied dose. This implies an overestimation of the maximal concentration in the groundwater for doses lower than 1 kg/ha and an underestimation for doses higher than 1 kg/ha.
The *fraction* left in the plough layer is assumed to be independent of the dose applied to the soil surface. Where the dose differs from the 1 kg/ha, the opposite effect is seen for accumulation as for the maximal concentration in the groundwater: the fraction left in the plough layer for doses lower than 1 kg/ha is underestimated and overestimated for doses higher than 1 kg/ha.

Serious underestimation of the maximal concentration in the deeper groundwater and overestimation of the fraction left in the plough layer may occur for very high substance

dose rates.

6.4 Time of substance load

Earlier studies have shown the accumulation and leaching to be sensitive on the time at which the substance is applied to the soil (*Van der Linden and Boesten, 1989*). Application in a relatively dry period will result in lower transport and leaching, and higher transformation (hence reduced leaching) than would be the case in a relatively wet period. In the latter case, leaching will be faster and leaching concentrations higher. Furthermore, at higher temperatures the transformation rate is higher and leaching lower, temperature is therefore a sensitive factor just after the time of substance application because transformation is optimal in the upper soil .

There are restrictions related to the period of sewage-sludge application in Groundwater Protection Areas. According to the code mentioned in 6.1 (Art. 18), application of sewage sludge in Groundwater Protection Areas in use as cultivated land, maize land or non-agricultural land is forbidden from September to January. In this study, application in spring has been considered because this concerns the most common form of agricultural practice which is legal.

7. SOIL-GROUNDWATER MODULE

7.1 Accumulation

In the Soil-Groundwater Module, accumulation is defined as the percentage of the amount of substance applied, along with the sewage sludge, left in the topsoil one year after sewage sludge application. For the topsoil layer a depth range of 20 cm has been considered, because:

- over this depth range a high root density is usually found and substance uptake by roots could be considerable;
- this depth range concerns the ploughing depth ('plough layer'), where substances over this depth range could reach the soil surface due to ploughing activities and direct human exposure is possible (dermal contact, ingestion).

7.2 Maximal concentration in the deeper groundwater

In the Soil-Groundwater Module, leaching affinity is represented by the maximal concentration in the deeper groundwater. If the maximal concentration has not been reached after 10 years, the quality of the groundwater is not considered because accumulation is higher than leaching.

7.3 Procedure

As has been discussed in detail in the previous chapters, it is possible to calculate the accumulation in the topsoil layer and the maximal concentration in the deeper groundwater for each substance with the help of the PESTLA model. Based on a standard environment only two substance-specific parameters have to be known:

- the K_{om} (see Section 2.4) and
- the DT_{50}-soil (see Section 2.5).

The PESTLA model uses a variable time step, of which the magnitude varies from ca. a half an hour to one day, mainly depending on the rain/evaporation-dependent water fluxes in the upper soil compartment. As a consequence, several hundreds of time steps are needed to calculate accumulation and leaching for a period of only one year. Because this procedure places high demands on computer time, characteristic of numerical modelling for transient flow patterns in the unsaturated zone, the PESTLA model is too time consuming to explicitly incorporate it in the general DRANC.

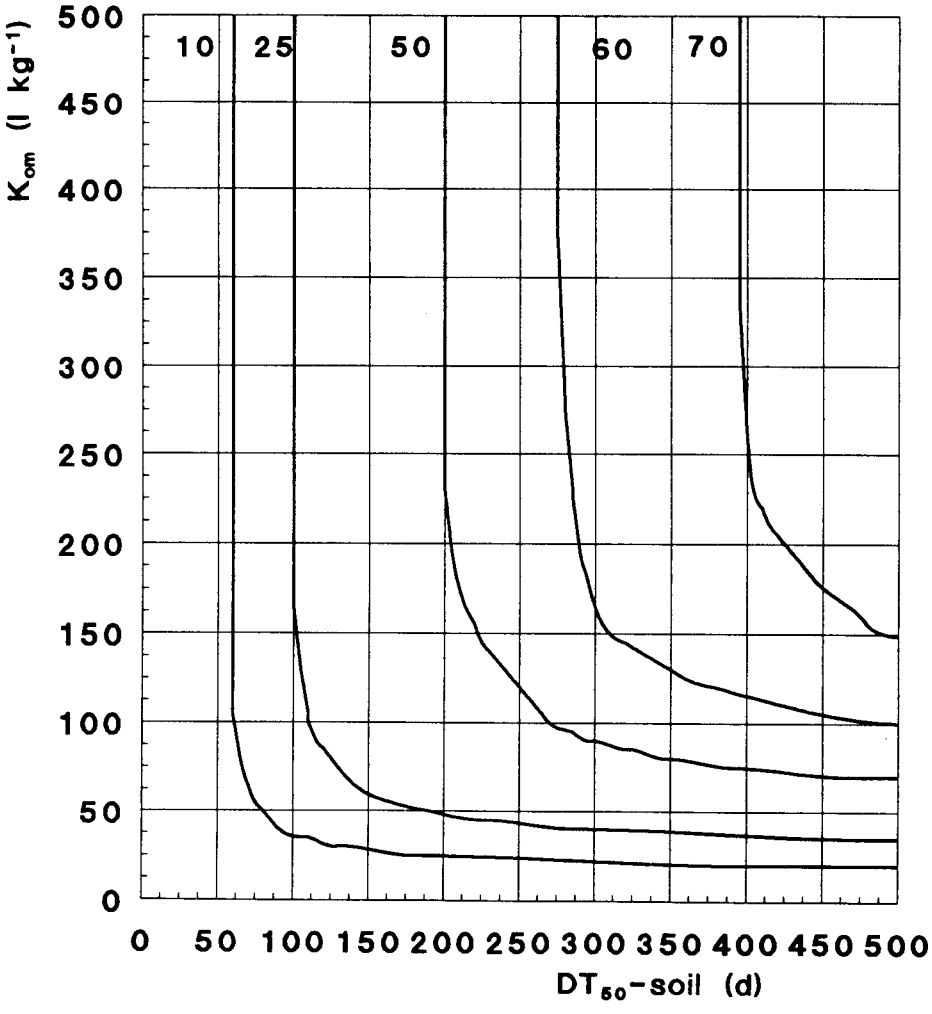

Figure 3: Iso-lines of equal accumulation (percentage of the dose left after one year) in the plough layer (0-0,2 m) as a function of K_{om} and DT_{50}-soil.

For this reason, the accumulation and maximal concentration in the deeper groundwater have been calculated, within the given range, for various combinations of K_{om} and DT_{50}-soil. In the Soil-Groundwater Module, the actual accumulation and maximal concentration in the deeper groundwater for a specific substance can be determined by table interpolation for the substance-specific K_{om} and DT_{50}-soil (linear interpolation), and multiplication by the actual substance dose rate, expressed as kg/ha.

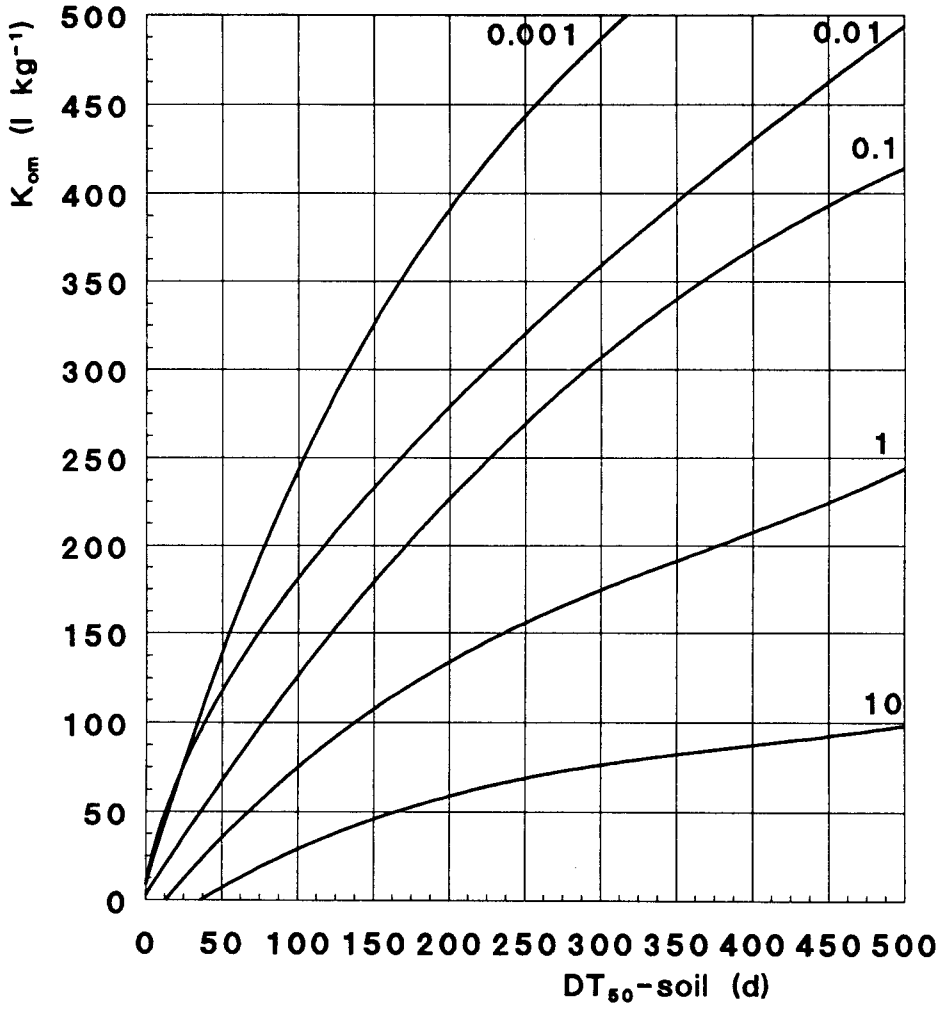

Figure 4: Iso-lines of equal maximal concentration in the deeper groundwater [ug/l] as a function of K_{om} and DT_{50}-soil.

The table showing calculated accumulation and maximal concentration in the deeper groundwater, serving as the basis for the Soil-Groundwater Module, is given in Appendix 2. Based on the analogy of the procedure for pesticide admission, the fraction of the applied dose that percolates into the uppermost groundwater is given in the table as well.

Iso-lines of equal accumulation (Figure 3) and equal maximal concentration in the deeper groundwater (Figure 4) can be constructed from the calculated values, with a spline interpolation program. Except for the numerical interpolation module, as incorporated in the DRANC, the nomograms provide a better understanding of the influence of the K_{om} and DT_{50}-soil on accumulation and the maximal concentration in the deeper groundwater. Furthermore, the nomograms allow visual interpretation of accumulation and maximal concentration in the deeper groundwater, for each substance.

7.4 Computer program

Recently, the procedure described above has been implemented in the DRANC, as part of the USES (Uniform System for the Evaluation of Substances), in the menu driven computer program (USES prototype II). The computer program has been described in detail in *Ministerie van Volkshuisvesting en Ruimtelijke Ordening et al., 1992.*

When applying the USES prototype II computerprogram, the following information is needed for the Soil-Groundwater Module:

- Substance characteristics:
  - . the sorption coefficient based on organic matter, K_{om}, to be determined with Eqn. 7, Section 2.4 and
  - . the half-life, DT_{50}-soil, to be determined with Eqn. 19, Section 2.5.3.
- The actual substance dose rate, as calculated in the Sewage Sludge Module, incorporated in the USES.

8. ACCURACY

An estimation of the accumulation and the maximal concentration in the deeper groundwater can be accomplished along the lines as the procedure as described in Section 7.3. Uncertainty exists in the determination of these parameters because of:

- uncertainty in the choice and description of the processes (conceptual model) and
- uncertainty in the assessment of the input parameters.

8.1 Conceptual model

In the unsaturated zone the relevant processes determining leaching and accumulation are fairly well known. Therefore, the concept that has been followed to calculate

- the accumulation in the topsoil layer one year after sewage sludge application and
- the maximal concentration in the *uppermost* groundwater

seems to be reasonable compared to the identification of the input parameters, which are characterized by a rather large variation (see, for example, *Jury et al., 1987*).

Less clear is the significance of the processes in the *saturated* zone. This implies uncertainty during the second step in the calculation of the maximal concentration in the deeper groundwater, where the change in concentration is calculated from the time the substance enters the saturated zone till it reaches the drinking-water abstraction depth. In the light of the fairly long resident times, neglecting sorption and transformation in the saturated zone could lead to overestimation of the maximal concentration in the deeper groundwater.

Furthermore, in translating the maximal concentration in the uppermost groundwater into the maximal concentration in the deeper groundwater, dispersion and diffusion have not been accounted for. Due to the non-linearity of these processes no simple formula can be derived to include smearing the front due to dispersion and diffusion. *Wessolek et al. (1989)* found by experiment a decrease in the concentration peak of about 30% for a fine-

medium sand, over a depth range of 10 m (unsaturated zone). Because the influence of dispersion/diffusion sharply decreases with a decreasing concentration gradient, the overestimation of the maximal concentration in the deeper groundwater due to neglecting these processes is probably not more than a factor of two.

The base flow in the unsaturated zone, which would result in dilution and hence a concentration decrease in the deeper groundwater, is characterized by a huge local variance on a large scale, like in the Netherlands. This variability cannot be accounted for with a one-dimensional model (if this variability can be quantified at all). Base flow will, on the basis of the worst-case approach, be omitted. Besides, this conforms to the non-location-specific character of the DRANC.

Furthermore, uncertainty results from the correction for the *actual* substance dose rate. The accumulation and maximal concentration in the deeper groundwater have been calculated for a (single pulse-type) substance dose of 1 kg/ha. The response for these parameters on the calculated amount of substance entering the soil, as calculated in the Sludge Module, is assumed to be linear. Because of the fact that sorption is taken as a (slightly) non-linear function of the liquid concentration, this simple linear relationship is not true. If $1/n < 1.0$, which is the case in this study ($1/n = 0.9$), linear interpolation will result in:

- an underestimation of the leaching and maximal concentration in the deeper groundwater and an overestimation of the accumulation for doses *higher* than 1 kg/ha;
- an overestimation of the leaching and maximal concentration in the deeper groundwater and an underestimation of the accumulation for doses *lower* than 1 kg/ha.

The uncertainty introduced by the linear response on the substance dose rate depends, in the first place, on the range of the dose, following from the Sludge Module, and could be important for high dose rates. In the future, if actual data for the dose have been calculated for several practical cases, the quantification of this uncertainty should be evaluated.

Finally, linear table interpolation is performed in the Soil-Groundwater Module, which

causes uncertainty. The magnitude of the resulting error is dependent on the position of the substance, represented by the DT_{50}-soil and the K_{om}, in the interpolation table (Appendix 2).

8.2 Input parameters

Sensitivity analysis has shown that the PESTLA model calculations, based on a 1 kg/ha substance dose rate, are, in decreasing order, especially sensitive to uncertainty in *(Boesten, 1991)*:

1. the sorption coefficient, K_{om} and the half-life, DT_{50}-soil and
2. the sorption exponent and rain surplus.

Note that sensitivity is strongly dependent on the characteristics of the specific substance under investigation. *Malkoç et al. (in press)* show large variations in atrazine leaching because of uncertainty of DT_{50}-soil and especially of the K_{om}.

Uncertainty results from the calculation of the K_{om} from the K_{ow}, where the empirical Karickhoff relation (Eqn. 5) has been used. However, the determination of the DT_{50}-soil in the unsaturated zone, based on the derivation of the DT_{50}-soil water from the DT_{50}-$water_{RB}$, probably provides more uncertainty because of some of the rough assumptions made. Especially the assumption that the transformation rate is proportional to the biomass is debatable. Except for the determination of the DT_{50}-soil from the DT_{50}-$water_{RB}$, uncertainty is introduced in the determination of the DT_{50}-$water_{RB}$ when the substance is not readily biodegradable, but some degradation has been registered during the 28 days of the test. In this case, the DT_{50}-$water_{RB}$ is determined by an extrapolation procedure, as described in Section 2.5.2, which implies more uncertainty when the extrapolation section is longer.

Although local surplus rainfall and evaporation data are usually available in the Netherlands no location-specific situation has to be considered in the DRANC. Besides, place and time-dependent rainfall/evaporation data will only imply significant uncertainty for some mobile substances, i.e. those with low K_{om}-values, *(Swartjes et al., in press)*.

Uncertainty is introduced by using an average value for the sorption coefficient of 0.9 (Eqn. 1) in the standard situation. This parameter is known to vary between 0.8 and 1.1 for a wide range of pesticides (*Van der Linden and Boesten, 1989*).

The choice of the fraction of the area infected by substance application, i.e. the choice of the areal fraction, causes uncertainty in the actuel exposure.

Finally, uncertainty results due to the calculation of the *actual* substance dose rate, as performed in the Sewage Sludge Module.

8.3 Overall accuracy

In Table 1 the uncertainty of the different sources, i.e. in some critical assumptions of the conceptual model and of the different input parameters, has been evaluated. Furthermore, it has been indicated in the table whether the identification of the sources will result in an overestimation or an underestimation of the exposure criteria (accumulation and maximal concentration in the deeper groundwater). Finally, an estimation has been made for the resulting uncertainty of the exposure criteria.

From Table 1 it can be seen that most assumptions that have been made result in an *overestimation* of the maximal concentration of the deeper groundwater (worst-case procedure). Taking this into account, it can be concluded that by using the Soil-Groundwater Module, a fair prediction can be made for the maximal concentrations of the deeper groundwater for the *worst-case* approach.

Furthermore, it is possible, in spite of several uncertain factors in the actual exposure, to give an indication of:

- the *actual* amount of substance in the uppermost soil one year after sewage sludge application (accumulation) and
- the *actual* maximal concentration in the *upper* groundwater.

A large amount of uncertainty is introduced by some assumptions made in the conceptual model concerning the saturated zone (source 1 - 4 in Table 1). Therefore, we can conclude that for the *actual* maximal concentration in the *deeper* groundwater only a rough estimate can be assessed.

Table 1: Uncertainty in the conceptual model, in the different input-parameters, and in the exposure criteria, i.e. in the accumulation (acc.) and in the maximal concentration in the deeper groundwater (mcgrw.)

NUMBER	SOURCE	UNCERTAINTY OF THE SOURCE	OVERESTIMATION/UNDER ESTIMATION	ESTIMATED UNCERTAINTY IN THE EXPOSURE CRITERIA
	CONCEPTUAL MODEL		acc.: mcgrw.:	
1.	Neglecting sorption in the saturated zone	high	- overest.	moderate
2.	Neglecting transformation in the saturated zone	high	- overest.	high
3.	Neglecting diffusion/ dispersion in the saturated zone	low	- overest.	low
4.	Neglecting base flow in the saturated zone	low	- overest.	low
5.	Multiplying by the actual substance dose rate, in kg/ha	low - high *1	both both	low - high *1
6.	Linear table interpolation	low - high *2	overest. overest.	low - high *2

Table 1 (continued): Uncertainty in the conceptual model, in the different input-parameters, and in the exposure criteria, i.e. in the accumulation (acc.) and in the maximal concentration in the deeper groundwater (mcgrw.)

NUMBER	SOURCE	UNCERTAINTY OF THE SOURCE	OVERESTIMATION/UNDERESTIMATION		ESTIMATED UNCERTAINTY IN THE EXPOSURE CRITERIA
	INPUT PARAMETERS		acc.:	mcgrw.:	
7.	K_{om} (from K_{ow}, Eqn. 5)	high	both	both	high
8.	DT_{50}-soil (from DT_{50}-$water_{RB}$, Eqn. 19)	high	both	both	high
9.	Sorption exponent, taken as 0,9 (average value)	high	both	both	high
10.	Actual substance dose rate	low - high *3	both	both	low - high *3
11.	Areal fraction	high	both	both	moderate

*1: dependent on the amount of substance in sewage sludge, as calculated in the Sewage Sludge Module

*2: dependent on the position in the interpolation table.

*3: dependent of the quality of the Sewage Sludge Module

9. CONCLUSIONS/ RECOMMENDATIONS

9.1 Conclusions

A new Soil-Groundwater Module has been developed that will be incorporated in the Dutch Risk Assessment System for New Chemicals. In this module

- the accumulation in the uppermost soil layer one year after sewage sludge application and
- the maximal concentration in the deeper groundwater

are used as criteria for determining the exposure of humans and the environment to new xenobiotic substances due to sewage-sludge application.

The accumulation of the substance in the topsoil layer and the maximal concentration in the uppermost groundwater are first explicitly calculated using the model PESTLA. In a second step the maximal concentration in the *deeper* groundwater has been determined by a simple analytical procedure.

Accumulation and maximal concentration in the deeper groundwater have been calculated for various combinations of K_{om} and DT_{50}-soil for a single pulse type application dose of 1 kg/ha. For a specific substance and specific substance dose rate, accumulation and maximal concentration in the deeper groundwater are assessed in the Soil-Groundwater Module by an linear interpolation procedure and multiplication by the actual application dose rate, expressed as kg/ha. The sorption coefficient, K_{om}, has to be calculated from the n-octanol/water distribution coefficient, and the half-life, DT_{50}-soil, has to be derived from Readily Biodegradability test results. Equations are given to derive both input parameters. The calculation procedure has been incorporated in the menu driven computer program of the Risk Assessment System. When applying the program, the K_{om} and the DT_{50} are the only input parameters needed.

A prediction can be made for the maximal concentration in the deeper groundwater for the *worst-case*. An indication can be made for the *actual* accumulation, whereas for the *actual*

maximal concentration in the deeper groundwater a rough indication is possible.

9.2 Recommendations

There are indications that sorption and/or transformation play a role of importance for a number of organic substances in the water-saturated zone. It should be stressed that due to the relatively long resident times in the saturated zone, even low transformation rates can result in a large decrease of the concentration. Future developments concerning behaviour of organic substances in the water-saturated zone should be followed. Possible new insights might lead to implementation of these processes in the DRANC and hence to retarded transport in the saturated zone, and in lower maximal concentration in the deeper groundwater.

For future improvement of the accuracy of the Soil-Groundwater Module the sensitivity of the following processes and extensions to the model might be subject of research:

A worst-case situation for leaching, i.e. a sandy soil with poor organic matter content and a phreatic aquifer, has been considered.

1. Accumulation could be based on a different worst-case soil, i.e. a clayey soil with high organic matter content.

Substance load, due to sewage sludge application, has been assumed to take place at a fixed time, i.e. spring.

2. Accumulation and leaching could be determined for any other application time.

No dilution processes other than vertical mixing of polluted and clean groundwater has been accounted for during transport from the uppermost groundwater to the groundwater abstraction well.

3. The role of the substance-front smearing and peak value reduction due to diffusion and dispersion could be investigated.

Accumulation and quality of the deeper groundwater have been considered for a pulse-type single-dose substance application due to sewage sludge.

4. Along the lines of the overall DRANC, any other kind of application scheme, like continuous, repeated application, or combined continuous/ repeated application could be dealt with.

The response of accumulation and maximal concentration in the deeper groundwater to the substance dose rate has been assumed to be linear.

5. More complex dose-response functions could be investigated for the actual substance dose rate resulting from the Sludge Module. For this reason, if actual data for the substance dose application have been calculated in the Sludge Module for several practical cases in the future, the quantification of this uncertainty should be evaluated.

To assess accumulation and maximal concentration in the deeper groundwater a linear interpolation procedure for the sorption coefficient, K_{om}, and the half-life, DT_{50}, has been incorporated.

6. More complex interpolation procedures could be investigated in the Soil-Groundwater Module.

Some rough assumptions have been made for calculating the half-life in soil, DT_{50}-soil, from the half-life, DT_{50}-$water_{RB}$, in water from the Readily Biodegradability. Especially the assumption that transformation rate is proportional to biomass is rather debatable.

7. More accurate methods to determine the DT_{50}-soil from the DT_{50}-$water_{RB}$ could be investigated.

No ecotoxicological features or implications for grazing cattle have been directly accounted for in the Soil-Groundwater Module.

8. The ecotoxicological response of earthworms to exposure to the substance on a small and/or larger time scale could be implemented in the future. Knowledge about behaviour of earthworms in soil and about ecotoxicological criteria should then be provided for by the ecotoxicologists. Furthermore, exposure to the

substance could be assessed for grazing cattle.

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APPENDIX 1: LIST OF DEFINITIONS AND SYMBOLS

- Areal fraction: fraction of groundwater capture zone under sewage-sludge application [-].

- Base flow : standard groundwater transport in the aquifers, characterised by a dominant horizontal waterflow component.

- BOD : Biochemical Oxygen Demand.

- CFU : colony forming units [-].

- Convection : solute movement along with the moving water mass.

- c_l : concentration in the liquid phase [M L^{-3}].

- c_s : content in the solid phase [M L^{-3}].

- $c_{u,max}$: concentration in the uppermost groundwater (groundwater in the saturated zone, direct under the unsaturated zone) [M L^{-3}].

- $c_{d,max}$: maximal concentration in the deeper groundwater, at the depth of the drinking water abstraction well [M L^{-3}].

- c_{tot} : total substance concentration [M L^{-3}].

- Dispersion : solute movement, caused by inhomogeneous soil structural features.

- Diffusion : solute movement within the water phase, due to a concentration gradient; aims at minimal free energy.

- DOC : Dissolved Organic Carbon.

- DT_{50}-soil : half-life: time needed to reduce the amount of a substance in soil by transformation, to 50 % [T].

- DT_{50}-soil water : half-life in the liquid phase of the soil [T].

- DT_{50}-$water_{RB}$: half-life in water for an RB test [T].

- f_i : areal fraction [-].

- f_{oc} : fraction organic carbon [-].

- f_{om} : fraction organic matter [-].

- k : transformation rate coefficient [T^{-1}].

- K_d : distribution coefficient [L^3 M^{-1}].

- K_f : Freundlich sorption coefficient [L^3 M^{-1}].

- K_{oc} : sorption coefficient based on the organic carbon content in the soil [L^3 M^{-1}].

- K_{om} : sorption coefficient based on the organic matter content in the soil [L^3 M^{-1}].

- K_{ow} : n-octanol/water distribution coefficient, representing the ratio of a substance in n-octanol and water [-].

- 1/n : Freundlich exponent [-].

- phreatic groundwater : groundwater in aquifers which are not protected subtraction by an overlaying clay layer and are in hydrostatic equilibrium with the atmosphere.

- R_{tr} : transformation rate [M L^{-3} T^{-1}].

- DRANC : Dutch Risk Assessment System for New Chemicals.

- RB : see "Readily biodegradability test".

- Readily biodegradable : see "Readily biodegradability test".

- "Readily biodegradability test" (RB) : standardized transformation test: if a substance is "readily biodegradable" the substance will be largely mineralized within a period of 10 days (determination by measuring CO_2, O_2 or DOC) under aerobic conditions.

- Sorption : reversible physical/chemical interaction between substances in the soil liquid and solid phase.

- t : time [T].

- Transformation : Irreversible conversion of a substance, due to (micro-)biological processes and/or abiotic degradation.

- ρ : density of soil solid phase [M L^{-3}].

- θ : water content [L^3 L^{-3}].

APPENDIX 2: TABLE: ACCUMULATION AND MAXIMAL CONCENTRATION IN THE DEEPER GROUNDWATER AS A BASIS FOR THE SOIL-GROUNDWATER MODULE IN THE DUTCH RISK ASSESSMENT SYSTEM OF NEW CHEMICALS

DT_{50}-soil : Half-life in soil (d)

K_{OM} : Sorption coefficient, based on organic matter content (l/kg)

$c_d$max : Maximal concentration in deeper groundwater (µg/l), *for a substance dose of 1 kg/ha*

%PER : Percentage of dose leached below a depth of 1 m *for a substance dose of 1 kg/ha*

%ACC : Percentage of dose still present in topsoil (0-0.2 m) *for a substance dose of 1 kg/ha* after a period of one year

DT_{50}-soil	K_{OM}	$C_d$max	%PER	%ACC
0.0	0.0	0.0000	0.000	0.000
5.0	0.0	0.0225	0.003	0.000
10.0	0.0	0.3100	0.120	0.000
20.0	0.0	3.1900	1.270	0.000
40.0	0.0	14.2000	5.710	0.000
60.0	0.0	24.4000	9.880	0.000
80.0	0.0	32.3000	13.100	0.000
100.0	0.0	38.3000	15.600	0.000
150.0	0.0	48.2000	19.600	0.000
200.0	0.0	54.1000	22.100	0.000
300.0	0.0	60.8000	24.814	0.001
400.0	0.0	64.4600	26.332	0.001
500.0	0.0	66.7700	27.240	0.001
0.0	10.0	0.0000	0.000	0.000
5.0	10.0	0.0000	0.000	0.000
10.0	10.0	0.0073	0.003	0.000
20.0	10.0	0.8056	0.320	0.000
40.0	10.0	8.9600	3.870	0.170
60.0	10.0	20.3800	9.140	0.440
80.0	10.0	30.8000	14.210	0.700
100.0	10.0	39.4900	18.630	0.930
150.0	10.0	55.0300	26.930	1.350
200.0	10.0	64.9600	32.510	1.620
300.0	10.0	76.7100	39.390	1.950
400.0	10.0	83.3500	43.412	2.150
500.0	10.0	87.6100	46.042	2.270
0.0	20.0	0.0000	0.000	0.000
5.0	20.0	0.0000	0.000	0.000
10.0	20.0	0.0006	0.000	0.000
20.0	20.0	0.2137	0.082	0.035
40.0	20.0	3.9800	1.750	0.680
60.0	20.0	10.4600	5.225	1.830
80.0	20.0	16.9600	9.310	2.980
100.0	20.0	22.9210	13.370	4.000
150.0	20.0	35.6600	22.180	5.920
200.0	20.0	44.8000	28.900	7.200
300.0	20.0	56.7500	38.085	8.760

DT_{50}-soil	KOM	$C_d$max	%PER	%ACC
400.0	20.0	64.0300	43.903	9.650
500.0	20.0	68.9200	47.888	10.240
0.0	40.0	0.0000	0.000	0.000
5.0	40.0	0.0000	0.000	0.000
10.0	40.0	0.0000	0.000	0.000
20.0	40.0	0.0067	0.003	0.008
40.0	40.0	0.3700	0.210	1.770
60.0	40.0	1.6700	1.090	4.960
80.0	40.0	3.8700	2.670	8.290
100.0	40.0	6.5400	4.720	11.270
150.0	40.0	13.6000	10.630	16.980
200.0	40.0	19.8000	16.440	20.800
300.0	40.0	29.0010	26.055	25.550
400.0	40.0	35.0900	33.182	28.300
500.0	40.0	39.3400	38.523	30.080
0.0	60.0	0.0000	0.000	0.000
5.0	60.0	0.0000	0.000	0.000
10.0	60.0	0.0000	0.000	0.000
20.0	60.0	0.0001	0.000	0.100
40.0	60.0	0.0410	0.025	2.510
60.0	60.0	0.3460	0.230	7.220
80.0	60.0	1.0200	0.780	12.220
100.0	60.0	2.0100	1.680	16.750
150.0	60.0	5.3100	5.060	25.500
200.0	60.0	8.8900	9.150	31.400
300.0	60.0	15.2300	17.171	38.760
400.0	60.0	20.1110	23.970	43.030
500.0	60.0	23.7500	29.476	45.820
0.0	80.0	0.0000	0.000	0.000
5.0	80.0	0.0000	0.000	0.000
10.0	80.0	0.0000	0.000	0.000
20.0	80.0	0.0000	0.000	0.116
40.0	80.0	0.0053	0.003	2.950
60.0	80.0	0.0700	0.055	8.610
80.0	80.0	0.2800	0.240	14.700
100.0	80.0	0.6800	0.630	20.200
150.0	80.0	2.3500	2.470	31.000
200.0	80.0	4.4100	5.170	38.400
300.0	80.0	8.4800	11.304	47.500
400.0	80.0	12.0330	17.140	52.830
500.0	80.0	14.9300	22.189	56.310
0.0	100.0	0.0000	0.000	0.000
5.0	100.0	0.0000	0.000	0.000
10.0	100.0	0.0000	0.000	0.000
20.0	100.0	0.0000	0.000	0.120
40.0	100.0	0.0007	0.000	3.190
60.0	100.0	0.0163	0.013	9.420
80.0	100.0	0.0877	0.079	16.180
100.0	100.0	0.2434	0.245	22.370
150.0	100.0	1.0245	1.230	34.440
200.0	100.0	2.2330	2.960	42.700
300.0	100.0	5.0500	7.434	52.990
400.0	100.0	7.6800	12.148	59.010
500.0	100.0	9.8700	16.466	62.950
0.0	150.0	0.0000	0.000	0.000
5.0	150.0	0.0000	0.000	0.000
10.0	150.0	0.0000	0.000	0.000
20.0	150.0	0.0000	0.000	0.126
40.0	150.0	0.0000	0.000	3.430
60.0	150.0	0.0005	0.001	10.300
80.0	150.0	0.0049	0.005	17.800
100.0	150.0	0.0210	0.025	24.700
150.0	150.0	0.1600	0.232	38.300
200.0	150.0	0.4800	0.775	47.700
300.0	150.0	1.4800	2.580	59.340

DT_{50}-soil	KOM	$C_d$max	%PER	%ACC
400.0	150.0	2.7140	4.941	66.190
500.0	150.0	3.9500	7.365	70.680
0.0	200.0	0.0000	0.000	0.000
5.0	200.0	0.0000	0.000	0.000
10.0	200.0	0.0000	0.000	0.000
20.0	200.0	0.0000	0.000	0.126
40.0	200.0	0.0000	0.000	3.490
60.0	200.0	0.0000	0.000	10.540
80.0	200.0	0.0003	0.000	18.290
100.0	200.0	0.0021	0.003	25.470
150.0	200.0	0.0285	0.047	39.600
200.0	200.0	0.1153	0.216	49.300
300.0	200.0	0.5000	0.863	61.510
400.0	200.0	1.0840	1.882	68.670
500.0	200.0	1.7400	3.026	73.360
0.0	300.0	0.0000	0.000	0.000
5.0	300.0	0.0000	0.000	0.000
10.0	300.0	0.0000	0.000	0.000
20.0	300.0	0.0000	0.000	0.130
40.0	300.0	0.0000	0.000	3.520
60.0	300.0	0.0000	0.000	10.670
80.0	300.0	0.0000	0.000	18.600
100.0	300.0	0.0000	0.000	25.900
150.0	300.0	0.0011	0.002	40.340
200.0	300.0	0.0081	0.011	50.350
300.0	300.0	0.0672	0.081	62.840
400.0	300.0	100.0	0.218	70.200
500.0	300.0	100.0	0.397	75.020
0.0	400.0	0.0000	0.000	0.000
5.0	400.0	0.0000	0.000	0.000
10.0	400.0	0.0000	0.000	0.000
20.0	400.0	0.0000	0.000	0.130
40.0	400.0	0.0000	0.000	3.520
60.0	400.0	0.0000	0.000	10.700
80.0	400.0	0.0000	0.000	18.640
100.0	400.0	0.0000	0.000	26.010
150.0	400.0	0.0000	0.000	40.560
200.0	400.0	100.0	0.001	50.645
300.0	400.0	100.0	0.006	63.240
400.0	400.0	100.0	0.019	70.660
500.0	400.0	100.0	0.200	75.530
0.0	500.0	0.0000	0.000	0.000
5.0	500.0	0.0000	0.000	0.000
10.0	500.0	0.0000	0.000	0.001
20.0	500.0	0.0000	0.000	0.120
40.0	500.0	0.0000	0.000	3.520
60.0	500.0	0.0000	0.000	10.710
80.0	500.0	0.0000	0.000	18.670
100.0	500.0	0.0000	0.000	26.060
150.0	500.0	100.0	0.000	40.660
200.0	500.0	100.0	0.000	50.780
300.0	500.0	100.0	0.000	63.420
400.0	500.0	100.0	0.001	70.880
500.0	500.0	100.0	0.010	75.770