Scenario analyses Dommel

Impact of sedimentation in the Dommel flood plain on heavy metal availability and bioaccumulation in flora and fauna

RWS RIZA report 2007.014

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Colofon

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Summary

This report describes the application of the BioChem-DSS, being developed in the EU KP6-programme AquaTerra, BASIN R3 work package, with the aim to assist in the definition and improvement of management options for the Meuse region.

A case study was carried out in a flood plain site of the river Dommel, a tributary to the Meuse. The present T0-situation was established, and the chemical and toxicological effects of sedimentation resulting from flooding events were investigated.
In the T1 scenario, the sedimentation of 10 cm of Dommel sediment was simulated. The quality of the suspended solids in the Dommel is very poor. As, Cd, Cu, Ni, Pb, Zn concentrations all exceed the quality standards for soil ("Intervention value") by some factors. In the T2 scenario, sedimentation was simulated when the metal load of the Eindergatloop, discharging into the Dommel, would be reduced to zero.

Plant uptake did not differ much between scenarios, which was expected because the deposited layer is too small to achieve physical contact between the sediment and the roots of most plants. For monocotyls however, some differences occur. Internal contents of the shoots are doubled from 0.15 mg/kg dw in the T0-scenario to 0.31 mg/kg dw in the T1-scenario. Grasses are a preferred food category for most herbivores, and may therefore impose a significant contribution to the dietary uptake of cadmium. Cadmium and zinc are effectively accumulated by willow. Dicotyls take up copper in larger amounts. It is apparent that actual risks at the Borkel site depend on the type of land use and habitat, and key species that may occur or are foreseen in future redevelopment situations.

The largest body concentrations for invertebrates will occur with scenario T1. Metal accumulation is a factor 2 (Cd, worm) to 7 (Zn, isopod) larger than in the present T0 situation. For the T2 scenario, body concentrations are lower than for the T1 scenario, but are still elevated in comparison to the present T0 situation.

1. Introduction

The Dommel sub-catchment area struggles with some environmental issues concerning the large scale contamination of heavy metals. These issues were made more explicit by the Water board the Dommel and the government organisation 'Actief Bodembeheer de Kempen' (ABdK), responsible for the development of management options for the Kempen region. The Dommel sub-catchment constitutes a major part of this region. Besides emissions of manure from agricultural sources, a historical pollution of heavy metals from zinc factories is one of the main problems in this region. The emissions from factories in the Dutch part of the Kempen region have been cut off in the last century, but at present a factory in the Belgian Kempen still emits large quantities of heavy metals, mainly through the Dommel river. This contributes to a large extent to the issues at stake, mentioned below.

A number of measures have been taken or will be taken in the near future to create a higher water retention volume in the upstream Dommel catchment during high river discharge periods. Among the measures considered are a partial blocking of the river Aa tributary (increasing the water level of the Aa), restoring of the meandering nature of the Dommel river and creation of retention areas for water storage. These measures must be regarded in relation to redevelopment projects in the Meuse river, that may lead to a (temporarily) hampered discharge of the Dommel into the Meuse.

- For the assignment and arrangement of these water storage areas a reliable prediction of quantity and quality of water and transported sediment is necessary. This determines the loading of flooded areas with contaminated suspended material that remains behind after settling. One of the main parameters to be investigated in this respect is the flooding frequency and average flooding duration (also depending on the local situation, such as the presence of depressions). Another important question is the quantity and quality of the Dommel suspended material and bedload transported from Belgium as a function of the river discharge (what happens under high discharge conditions?). Also insight in the chemical and biological availability of the metals is relevant for the evaluation of the actual risks (e.g. for grazing cattle), assessment of compensation claims and the identification of potential management options.
- The effect of suspended matter sedimentation and resuspension on the water quality determines the efficacy of measures like the installation of sediment traps. A new sediment trap in the Belgian Dommel system will be installed in the near future. At present, a sediment trap in Eindhoven is being partially dredged to restore its functionality. During this operation 200,000 m^3 (out of a total amount of 500,000 m^3) is removed by dredging. The quality of the dredged material (even after separation of the sludge fraction) is so poor, that it cannot be used as a construction material without an immobilisation treatment.

- Quantification of actual spreading of heavy metals through the Dommel water system (groundwater, sediment, surface water) and the trends in the (near) future is necessary for the evaluation of risks to be expected. More specifically: how tight are these metals bound to soil particles in seeping groundwater, what is the binding capacity of the soil and the sediment, how fast is the exchange process of metals between sediment and surface water?

One part of these issues is addressed in separate research activities, another part is addressed in the AquaTerra Trend 1, Trend 2, Flux 3 and BGC 3 work packages. For some of the quality issues, the BioChem decission support system (BioChem-DSS) could well provide relevant answers (Joziasse *et al.*, 2005).

This report describes the application of the BioChem-DSS, being developed in the Basin R3 work package, with the aim to assist in the definition and improvement of management options for the region.

2. BioChem functional design

2.1 General description

The BioChem-DSS was specifically designed for the prediction of heavy metal availability in floodplain sediments under varying environmental conditions (e.g. redox potential). It consists of a chemical speciation module and an ecotoxicological module. The functional and structural design of the model have been described in earlier deliverables (R3.2, R3.8 and R3.9). The chemical speciation module aims at the prediction of pore water concentrations (chemical availability) for several types of scenarios. These scenarios can be defined in terms of inundation patterns (determining the redox condition), soil composition, layer thickness, vegetation types, etc.

The chemical speciation module is based on the kinetics of soil chemical processes that determine the chemical availability of heavy metals (free ion activity of metals in the pore water). It can be used at two levels, a quick scan mode and an expert level mode, differing in expertise level needed.

Pore water concentrations calculated in the chemical speciation module are used as input data for the ecotoxicological module. This module calculates the uptake by biota, both flora and fauna. The ecotoxicological module quantifies the biological availability of metals using transfer functions for the different biota studied. The scientific background for the use of these transfer functions is given in deliverable R3.14 of the KP6-EU programme AquaTerra.

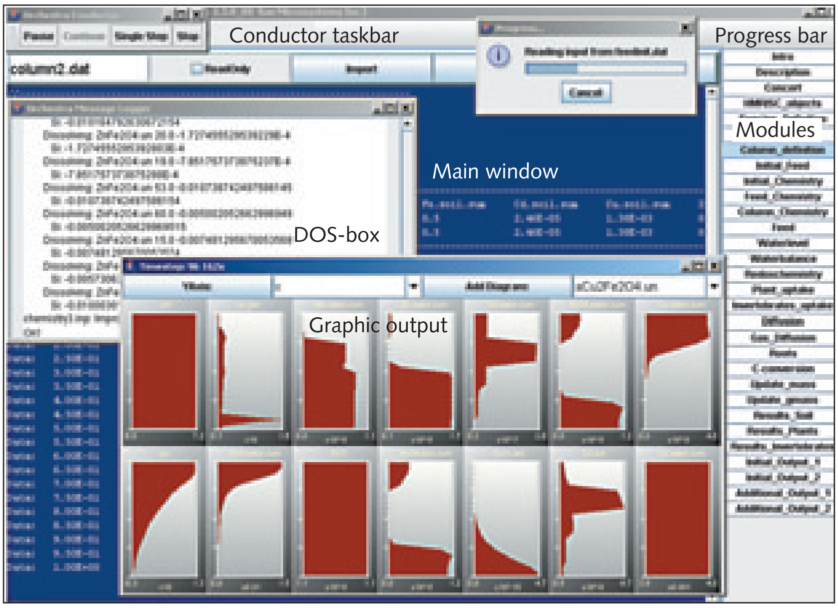
2.2 Functional design

2.2.1. Chemical module

BioChem is a soil chemical model that calculates the solid-solution partitioning and speciation of heavy metals in the embanked floodplain soils of the Dutch part of the Meuse and Rhine river system. It is designed as a part of the BioChem-DSS (Vink and Schröder, 2006; Vink and Meeussen, 2006) and follows the philosophy of high flexibility by a modular setup. Furthermore, it includes the functionality's described in CHARON+ (Vink *et al.*, 1999). BioChem is coupled to ORCHESTRA (Meeussen, 2003), an object-oriented framework for the calculation of speciation and adsorption processes programmed in JAVA.

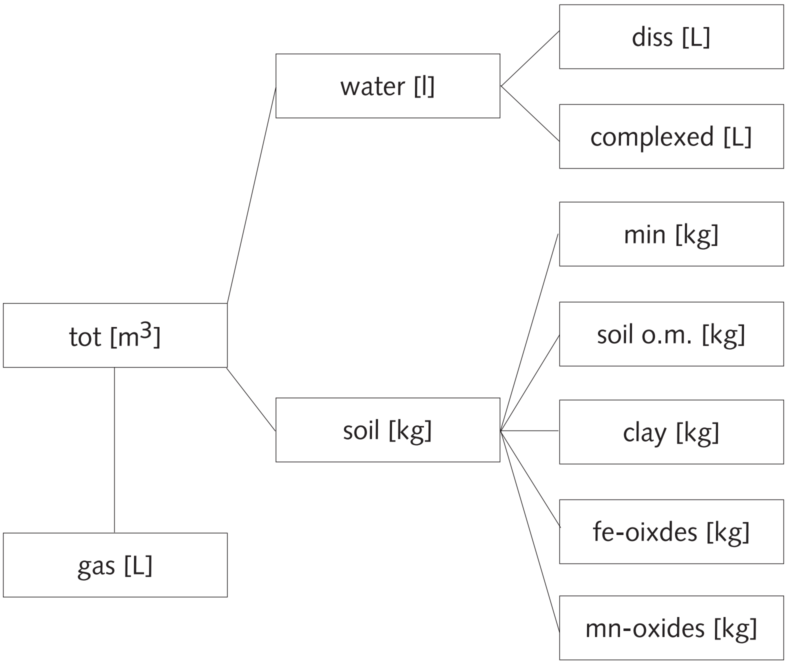
BioChem calculates the chemistry of a single, one-dimensional soil column. The column is divided into different layers (*nodes*). The nodes have a fixed surface area of 1m by 1m. For the vertical resolution a 0.05m layer thickness is standard, but different resolutions can be defined. Soil column properties are imported via the tabs Column_definition (column2.dat).

Figure 1
Structure of BioChem windows



Components, species and minerals

Species can be present in different phases. BioChem uses the following phase system:



tot is the total volume of the system, *water, gas,* and *soil* are the water phase, gas phase and the solid soil matrix, respectively. diss represents all dissolved species in the water phase and *suspended* the species complexed by the soluble fraction of organic carbon (DOC). Likewise, *min* represents all minerals in the soil phase, *solid* the soil organic matter fraction; *clay, feoxides,* and *mnoxides* the clay , ironoxide, and manganese oxide fractions.

This separation makes it possible to generate output not only for individual species, but also for the total amount present in a phase. E.g. *Cd.min.sum* is the total amount of Cd in the mineral phase, *Cd.diss.sum* the sum of all soluble Cd species in the water phase and *Cd.mnoxides.sum* all Cd bound to manganese oxides. Similarly, we can define the model input in a very flexible manner, and are not limited to the component activity or total amount as input variable like in other chemical equilibrium models. E.g. when we have measured the concentration of Ca in a pore water sample, we can use the measured values directly by defining Ca.water.*sum* as an input variable instead of estimating an activity of Ca^{2+} which will approximate the measured total amount in the pore water sample.

Input files

The chemical properties of the soil system are defined in the Column_definition tab. This file contains the soil data ordered in a table format. Generally, for all components we must enter here a concentration or total amount to be able to calculate the speciation of the system:

component	input format	unit
H	H.act	[mol/l]
e	e.act	[mol/l]
Cl	Cl.water.sum	[mol/l]
NO_3	NO_3.water.sum	[mol/l]
CO_3	CO_3.water.sum	[mol/l]
Ca	Ca.water.sum	[mol/l]
SO_4	SO_4.soil.sum	[mol/kg]
Al	Al.soil.sum	[mol/kg]
PO_4	PO_4.soil.sum	[mol/kg]
Fe	Fe.soil.sum	[mol/kg]
Mn	Mn.soil.sum	[mol/kg]
Cd	Cd.soil.sum	[mol/kg]
Cu	Cu.soil.sum	[mol/kg]
Zn	Zn.soil.sum	[mol/kg]
Pb	Pb.soil.sum	[mol/kg]
AsO_4	AsO_4.tot.sum	[mol/m^3]

Note that AsO_4 must be entered as [mol/m^3] (= 1300* AsO_4 [mol/kg] at the given porosity and bulk density); this is necessary due to the smaller solid-solution partitioning coefficient of As at lower redox potentials.

Next to the component concentrations, the amount of dissolved and soil organic matter and the amount of clay can be defined here (*DOC* [kg/l], *SOC* [kg/kg] and *clay_content* [kg/kg]). The amounts of ironoxides and manganese oxides are coupled to the adjacent mineral phases and are therefore calculated automatically by the system.
In case an input variable is not defined in column2.dat, the model makes use of predefined values in column.dat.

Soil moisture content

BioChem makes use of a flexible system for the distribution of water in the soil column. Generally, the porosity is uncritical and therefore fixed to a value of 0.5 (l/l). In the saturated layers, θ_γ is constant and only present at a low value (1E-6) for numerical reasons.
At the surface, θ_w is set to a minimum value of 1E-6. In the unsaturated layers, the water saturation is described by a gamma function.
θ_w is calculated by

$$\theta_w = \begin{bmatrix} porosity\text{-}\mathrm{min}_{gas} & x \geq waterlevel \\ dx_{w2}^{\gamma w} x\ (porosity\text{-}\mathrm{min}_{water}) + min_{water}\text{-}min_{gas} & x < waterlevel \end{bmatrix}$$

and θ_w is

$$\theta_{g=}\ porosity\ -\theta_w$$

with

$$dx_{w1} = \begin{bmatrix} {}^{x}/_{waterlevel} & waterlevel \leq 0 \\ 1 & waterlevel > 0 \end{bmatrix}$$

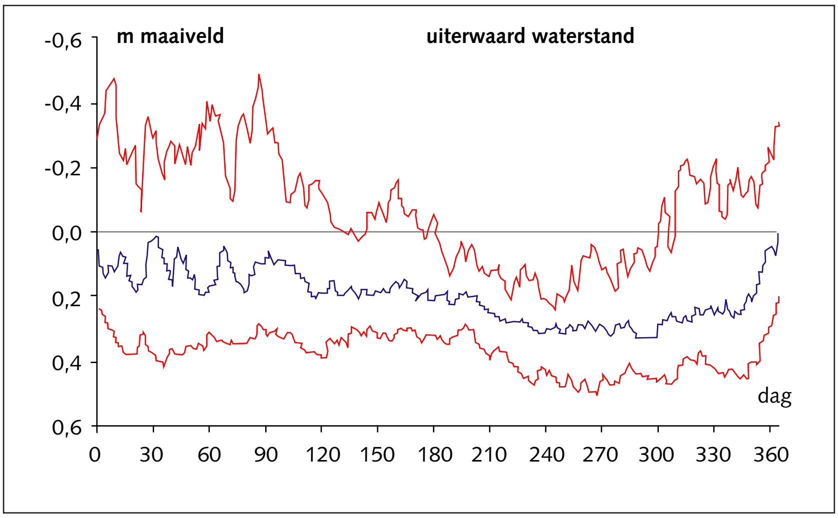
and

$$dx_{w2} = \begin{bmatrix} 0 & dx_{w1} < 0 \\ dx_{w1} & dx_{w1} \geq 0 \end{bmatrix}$$

Water level

The water level is read from an input file (waterlevel.dat) consisting of 365 values representing the daily water level [in m] below the surface. By using values explicitly defined in waterlevel.dat, BioChem can make use of real measurements, hydrological model predictions or interpolation of data from the DONAR database. Moreover, BioChem offers three generic scenarios, which represent a year with high water, a year with low water and an average year. Data are based on the water levels measured in Lobith in the years of 1985 to 2003. The data are converted to a water level in a given flood plain, its location indicated by river km according to the Dutch river indication system.

Figure 2
Three scenarios, based on Lobith waterlevel averages



Redox potential

The redox potential is related to the water level and the algorithm to calculate it is designed to fulfill a number of requirements:

- At the interface to the atmosphere $pe + pH = 20$
- At the interface of the saturated / unsaturated layer $pe + pH = 12$
- The rate of decrease of the redox potential in the profile can be adjusted to couple them to measured field data
- Above the groundwater table, the rate of decrease will depend on the groundwater table
- Below the groundwater table, the rate of decrease will be independent of the groundwater table

The algorithm makes use of a gamma function above the groundwater table and computes an exponential decrease of redox potential below the groundwater table:

$$\Delta pe = \begin{bmatrix} pH + 6 - 8 \times dx_{w1}{}^{\gamma} & x < waterlevel \\ 12x_e\left(-\alpha \times (x - waterlevel)\right)_{-pH} & x \geq waterlevel \end{bmatrix}$$

with

$$dx_{w1} = \begin{bmatrix} {}^{x}/_{waterlevel} & waterlevel > 0 \\ 0 & waterlevel \leq 0 \end{bmatrix}$$

and α representing the rate of change of the redox potential:

$$\alpha = -\frac{1.1}{dx_n}$$

The characteristic distance dx_n is given by the distance between the groundwater table and the layer with a *pe* of approximately -3.
The *pe* is calculated by

$$pe_t = pe_{t-1} + \frac{10}{365} * (pe_{t-1} - \Delta pe)$$

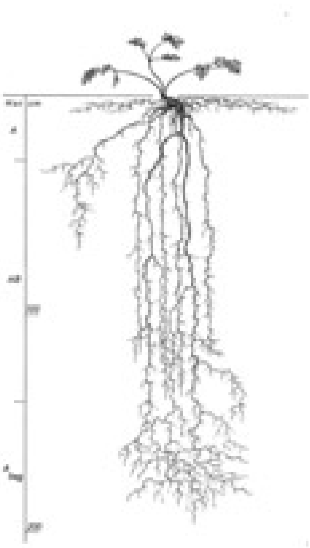
Alternatively, the pe can be calculated by oxidation reactions in the Roots and C_conversion tab (see section 2.2.2). However, the use of oxidation reactions for the calculation of the pe needs a careful balancing of oxidation and diffusion processes to avoid sudden jumps of the *pe* and the *pH*.

Diffusion

The modules Diffusion (diffusion.inp) and Gas_diffusion (gasdiff.inp) model diffusion processes in the water phase. In principle, for every component we can calculate diffusion in the water phase. However, diffusion is limited to dissolved component concentrations.
Diffusion makes use of Fick diffusion in the water phase, whereas Gas_diffusion describes the diffusion in the gas phase. For the latter, several approaches are possible which are discussed in the CHARON+ supporting reader. In the current version of BioChem we make use of

$$J_{gasdiffusion} = -4 * D_g * dC_g * \theta_g 3.1$$

Oxidation processes
BioChem contains two modules to represent oxidation processes. The first, C_conversion (c_conversion.inp) contains a general oxidation term comparable to the approach followed in CHARON+. With the second module Roots (roots.inp) a similar process can be applied to a limited layer, the root zone. Both modules offer the flexibility to define different formula to describe the oxidation processes, e.g. zero, first or second order reactions. However, mass balance changes are limited to the systems total amounts.
The use of two modules might be helpful to avoid the appearance of negative concentrations like in CHARON$^+$, which enables us to model realistic pCO_2 by simple algorithms.



2.2.2. Plant module

The plant uptake module calculates the cumulative and average concentration of a metal species or fraction in a predefined set of soil layers. This enables us to:

- Define the relevant root zone for a floodplain
- Choose the metal species or fraction which correlates best with metal uptake
- Define a time-dependent uptake behavior
- Calculate metal uptake in time

The plants are therefore divided into four groups:

1. Monocotyls (e.g., grasses)
2. Non-rhizobium forming dicotyls (most herbs)
3. Rhizobium forming dicotyls (e.g., clover)
4. Hyper-accumulators (e.g., willow)

The uptake of Cd, Cu, Zn by every group of plants is calculated by transfer functions, e.g.:

Cd_rhizobium.mg/kg = 0.07 – 0.0136 * pH + 7801 * DOC

To relate the plant uptake to a parameter that can vary in time, a cumulative average concentration can be calculated, e.g.

$$average\_Cd(t) = \sum_{nodes,t} \frac{Cd.water.sum(node,t)}{nodes*t}$$

In a comparable manner, the cumulative average concentration of every metal species or amount present in a phase can be defined and linked to the plant uptake. It is also possible to change the depth of the root zone by editing the number of nodes in the *Calculate plant uptake* task in the concert.xml file.

2.2.3. Invertebrates module

To link metal speciation to bioaccumulation, two types of transfer functions are implemented. These are based on differences in uptake routes by various organisms.

The first function is written for a group consisting of organisms having a highly permeable cuticle ("soft-bodied"), such as earthworms. The second group involves species having a firm exoskeleton ("hard-bodied"), such as isopods that have a chitin hardened calcium-rich carapax (epidermis). Bioaccumulation models are constructed using uptake and elimination kinetic parameters, in this way taking into account that in- and out- fluxes are distinctive processes due to various mechanisms like internal compartmentalization (redistribution of metals between reactive phases or organs). For both animal groups it was shown (Vijver, 2005) that simply using one of the metal species as input parameter is insufficient to cover all aspects of uptake. For that reason, two exposure routes, i.e. the dissolved fraction (dermal) and food (ingestion), are used as input parameters for the transfer function describing bioaccumulation in organisms.

In the next paragraphs, a short description of BioChem's transfer functions for soil>biota is given. For details we refer to Vijver (2005).

Soft-bodied species

For earthworms and related species, uptake and elimination can be described as a two-compartment model with first order kinetics. During exposure of earthworms to a polluted soil, accumulation in time (Cw(t) in µg/g) can be estimated according to equation 1 describing the first compartment and equation 2 describing the second compartment of the bioaccumulation.

$$Cw(t) = \frac{a}{k_2 + K_i}\left[1 - e^{-(k_2+k_i)t}\right] \qquad [1]$$

$$Cw(t) = \frac{k_i \cdot a}{k_2 + K_i}\left[(k_2 + k_i)t + e^{-(k_2+k_i)t} - 1\right] \qquad [2]$$

in which k_2 is the elimination rate constant (d^{-1}), ki is the rate constant for internal metal transfer from the loosely-bound metal compartment towards the storage compartment (d^{-1}), t is time in days. The parameter a represents metal uptake flux (= k_1 external metal concentration) separated in two fluxes either via the dermal or oral route, defined as:

$$a = k_1d\ [Me]_l + k_1o\ [Me]_x \qquad [3]$$

in which the first metal species $[Me]_l$ is representing the total pore water metal concentration (µg/L), d=dermal, o=oral. Output parameter from the chemical module is metal concentration (in µg/L) determined using 2.5 mM $CaCl_2$ extraction. The second metal species $[Me]_x$ represents metals that are bound to inorganic and organic ligands and bound to organic matter and that can be taken up under earthworm's gut conditions. In the chemical module total metal concentrations (in mg/kg) in the soil are measured by the metal concentration obtained using 0.43 M HNO_3 extraction.

The fraction of metal taken up via the dermal route is denoted D, and (1-D) is the fraction of metals available for uptake through the oral route. This relative contribution is the product of the uptake rate constants via the dermal and oral route and can be used as a check on the calculation of metal bioaccumulation in earthworms.

Hard-bodied species

For organisms having a firm exoskeleton, uptake and elimination can be described as:

$$Ci(t) = \frac{a}{k_2}\left[1- e^{-k_2 t}\right]\cdot\left[Fi + (1 - Fi)e^{-k_2(t)}\right] \qquad [4]$$

in which k_2 is the elimination rate constant (d^{-1}), t is time per day. Fi is the fraction (ranging from 0 - 1) that cannot be eliminated and is stored in the body. a is defined as the uptake rate flux, separated into a pool of metals taken up via soil and a pool taken up via food. Metal accumulation in isopods is for 50% from soil and 50% from food intake.

$$a = k_{1s}\,[Me]_x + k_{1f}\,[Me]_p \qquad [5]$$

where k_{1s} is the uptake rate constant from the soil (in g/g_{animal}/day) and k_{1f} is the uptake rate constant from the food (in g/g_{animal}/day). The metal species $[Me]_x$ represents the total metal concentration in soil (including metals bound to inorganic and organic ligands and bound to organic matter). Because litter and food are not accounted for in the chemical module, BioChem uses the output of the plant module (section 2.2.2) for a food source. The metal species $[Me]_p$ represents the metal concentration in litter, which for this purpose is equaled to the output from the plant module multiplied by a factor of 10.

The schematic model-route is chemical module → plant module → animal (hard-bodied). Transfer functions were derived for Cd and Zn.

It is assumed that isopods mainly feed on decomposed material of the group of dicotyledonous plants. Metal accumulation in plants differed from metal levels found in plant material subjected to decay (due to leaching, weathering, fragmentation). Although metal-specific, metal levels increase when plants become litter. Cd levels increase with a factor 5, Cu and Zn with a factor of 15, Pb with a factor 55, Fe with a factor 80. The concentration factor is set at a value of 10, which agrees with Ca concentration differences between fresh leaves and litter in a deciduous forest (Froment *et al.* 1969).

3. Definition off scenarios

3.1 Locations, available data and assumptions

For many soil characteristics, the BioChem model may use certain default values to act as best estimates in cases where these characteristics are not measured or unknown. The actual situation is, obviously, best described when actual measurements are used. For the scenario calculations that are performed in this study, a detailed and accurate dataset of on-site measurements is used.

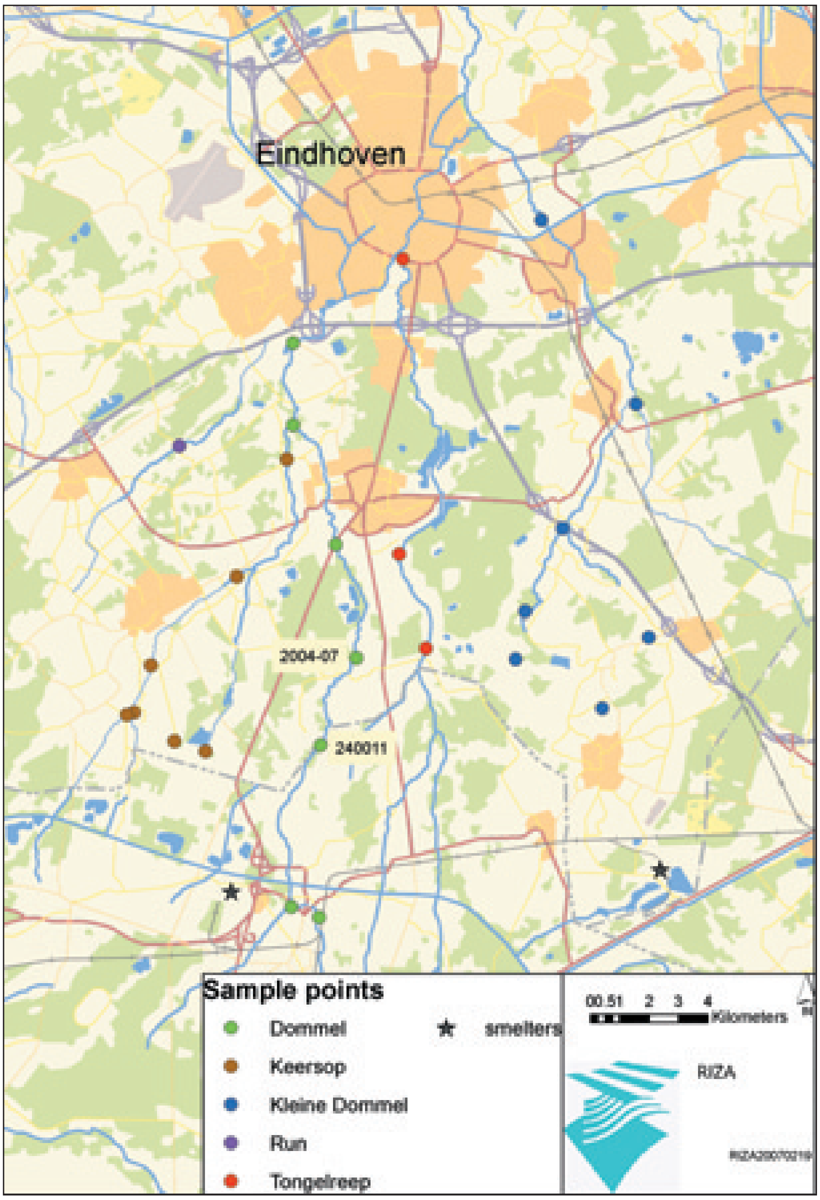
South of the city of Eindhoven, some water storage areas have been assigned. One of these areas is the nature reserve area between Valkenswaard and Borkel en Schaft, called "Malpie". This area is heavily contaminated with cadmium and zinc. Data of soil composition in the neighbourhood of this area are available for the upper 80 cm of four comparable sites. The dataset contains detailed information on soil matrix sizes, mineral composition, and degree of contamination. Also, measurements of surface water characteristics, among which the composition of suspended solids, are available.

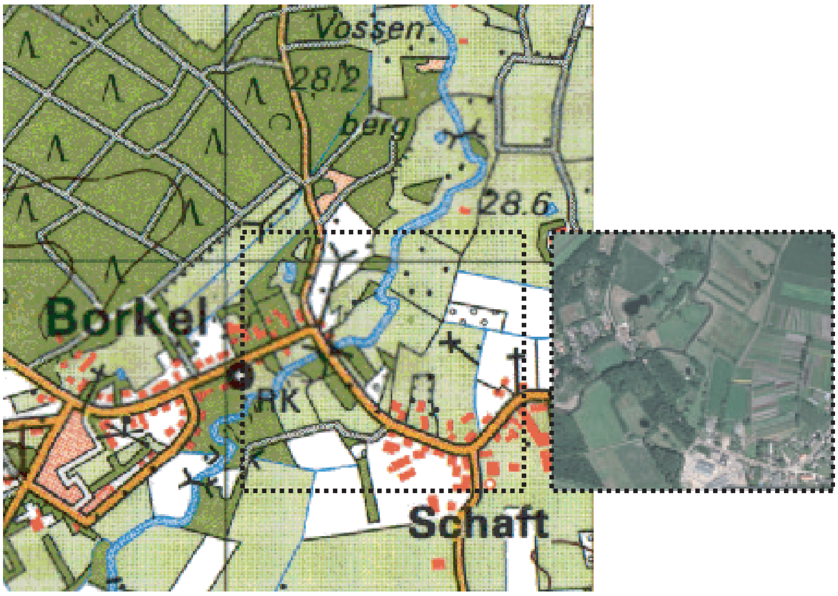
Table 1 (Chapter 4) summarizes characteristics of the 80 cm soil column, from here on called "Borkel" (location in Figure 4). Tables 2 and 3 summarize some characteristics of the suspended solids from the surface water of the Dommel. Detailed information is given in the appendix.

Figure 3

Nature reserve area Malpie

Figure 4
The Dommel tributary.
The simulated site Borkel is at location 2004-07 (X=159350; Y=367770). Geographic details are shown below. Suspended solids originate from location 240011: Grote Heide (X=157902; Y=364203).





3.2 Scenario definitions

Scenarios are defined as follows:

The T-0 scenario

The present situation. This scenario describes the actual situation of the flood plain soil on the Borkel site.

The T-1 scenario

This scenario describes the sedimentation of 10 cm of sediment from the Dommel river onto the flood plain soil. The characteristics and quality of this newly deposited layer equals the quality of suspended solids measured upstream at location Grote Heide. This scenario assumes unaltered land use.

The T-2 scenario

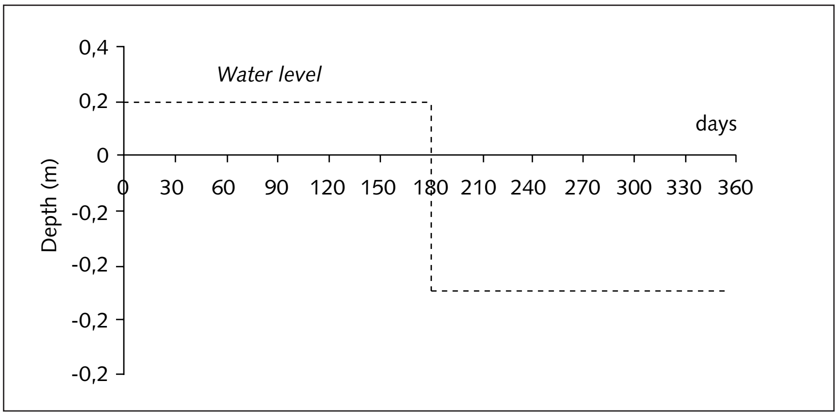
This scenario assumes that measures were taken to stop the emissions from the river Eindergatloop, discharging into the Dommel. This is reflected by measurements of suspended matter quality, obtained at location Neerpelt, right before the Eindergatloop discharges into the Dommel. Both the physical and the chemical properties of the suspended material are somewhat different. The T-2 scenario is calculated as in T-1, i.e. deposition of 10 cm sediment onto the flood plain.

Hydraulic scenario

Water balance and water level are kept uniform for all three scenarios. In order to simulate actual inundation, the water level is maintained at 20 cm above the soil surface for a period of 180 days. This period allows for sedimentation to take place. After this period, the water level is lowered to 50 cm below the soil surface, representing the average present situation.

Figure 5

Hydraulic scenario: water level over 1 year



4. Results

4.1 Present situation

Table 1 shows that the composition of the soil column – a clayey fluvisol - has a considerable variety with depth. Contaminant concentrations decrease with depth, showing in most cases their peak concentration in the 20-40 cm layer. Arsenic, cadmium and cobalt exceed MTR quality standards. Cobalt concentrations exceed MTR values up to a factor of 6, which is quite remarkable.
The quality of the suspended solids from the Dommel is very poor. As, Cd, Co, Cu, Ni, Pb, Zn concentrations all exceed MTR values, and in almost all cases (with the sole exception of Co) the Intervention value is exceeded by some factors. Of most concern however are the concentrations of Cd and Zn. These metals exceed Intervention values by a factor of 20 and 7, respectively. The origin of these metals is well known (zinc smelters from the Kempen area), and the widespread abundance is well documented. Of additional concern is the euthropic state of the surface water, illustrated by a high P content.

Table 1

Soil characteristics of the flood plain near Borkel (2004-07; X=159350; Y=367770; pH=7,32, SO_4=128,9 mg/l). Underlined values exceed MTR quality standards for sediment).

Depth cm	< 2um %	Tot C %	Al g/kg	Mn g/kg	Fe g/kg	P g/kg	Ca g/kg	Cr mg/kg	Ni mg/kg	Cu mg/kg	Zn mg/kg	As mg/kg	Mo mg/kg	Cd mg/kg	Pb mg/kg
0-20	13,4	3,47	25,7	0,241	44,8	1,39	0,85	37,2	9,8	7,69	90,5	221	0,52	5,18	67,3
20-40	20,1	3,04	27,3	0,125	78,9	1,67	1,02	40,5	17,6	8,23	173	521	0,81	15,8	73,8
40-60	15,8	2,03	31,9	0,095	102	7,25	2,09	46,9	17,1	4,31	390	359	0,64	6,01	18,6
60-80	13,3	1,76	43,1	0,067	9,5	0,22	2,30	57,7	10,7	5,4	30,5	8,5	0,28	0,32	14,2

Table 2

Suspended solid characteristics in the Dommel near Grote Heide (240011). These data are used for the T1 scenario.

Susp. solids	< 2um %	Tot C %	Al g/kg	Mn g/kg	Fe g/kg	P g/kg	Ca g/kg	Cr mg/kg	Ni mg/kg	Cu mg/kg	Zn mg/kg	As mg/kg	Mo mg/kg	Cd mg/kg	Pb mg/kg
	13,8	nd	nd	0,490	105,8	17,6	22,3	134,6	306,6	457,2	5171	251	14,9	237,8	930,6

It is clear that in both scenarios (T1 and T2) the quality of the top layer will decrease in any case. Total metal contents of the suspended sediment are for most elements several orders of magnitude larger than in the present top layer of the flood plain soil.

Table 3

Suspended solid characteristics in the Dommel near Neerpelt (without discharge of Eindergatloop). These data are used for the T2 scenario.

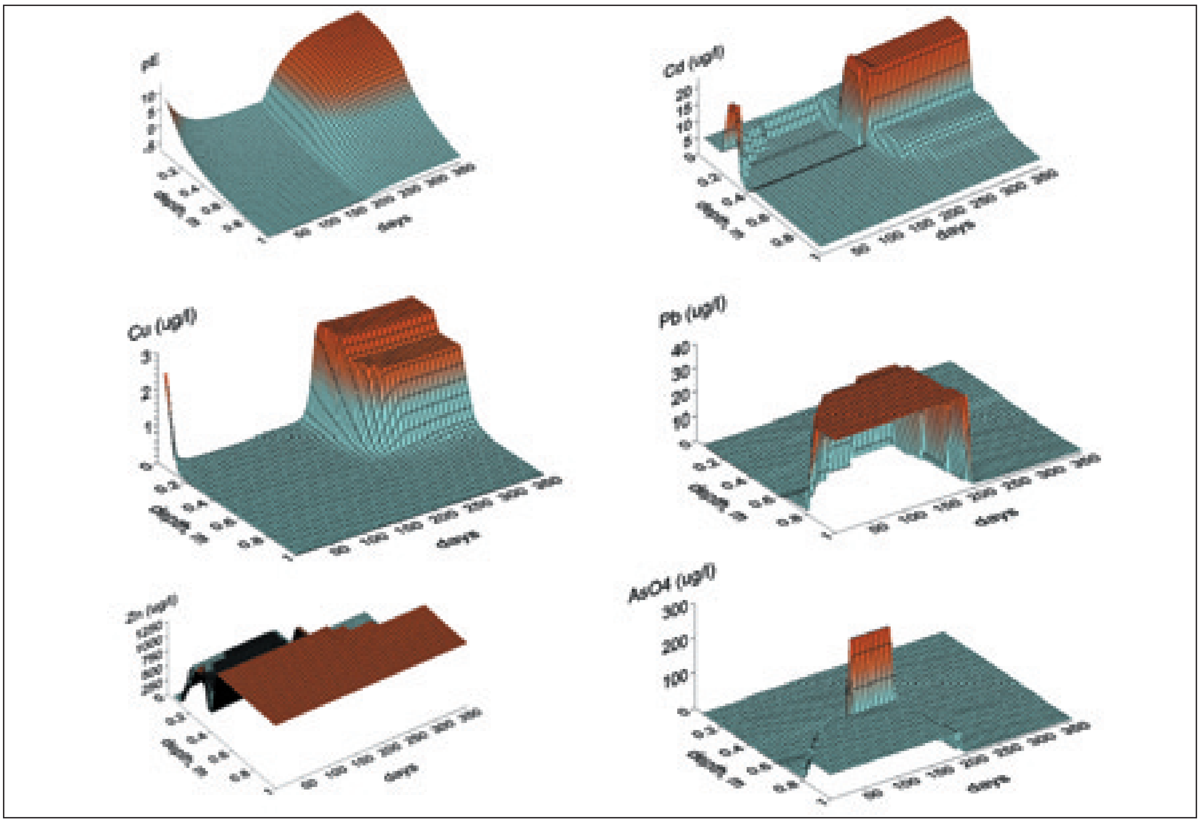
Susp. solids	< 2um %	Tot C %	All g/kg	Mn g/kg	Fe g/kg	P g/kg	Ca g/kg	Cr mg/kg	Ni mg/kg	Cu mg/kg	Zn mg/kg	As mg/kg	Mo mg/kg	Cd mg/kg	Pb mg/kg
	31	nd	nd	0,464	147,1	13,8	9,0	61,0	126,0	104,0	1783	200	5,0	13,0	112,0

Figure 6 shows the dynamic speciation calculation with the hydraulic scenario, specified in section 3.2, for the flood plain soil. Concentrations are dissolved fractions in pore water. The first graph shows the redox potential, expressed as pE. The period of inundation (0-180 days), followed by water drainage to a steady state situation of –0,5 m below surface, can be easily recognized.

The effect of the hydraulic movement is directly expressed in the chemical speciation. Oxidation of the soil leads to shifts in mineral composition. Especially the sulfides, iron oxyhydroxides and manganese oxides undergo major changes. As a result, sorption and complexation of metals and arsenic to soil components are affected. Cd, Cu, and Zn exceed MTR quality standards for surface water, while Pb and As concentrations decrease. Note that an inundation period of three months is the maximum time length to prevent arsenic from exceeding the MTR quality standards.

Figure 6

Time-depth concentration profiles (T0)



4.2 Chemical speciation for three scenarios

As explained in section 3.2, scenarios T1 and T2 simulate the deposition of 10 cm of suspended matter from the Dommel river of two respective quality classes (shown in Tables 2 and 3) onto the flood plain soil. The quantitative effects on chemical speciation are shown in Figure 7.

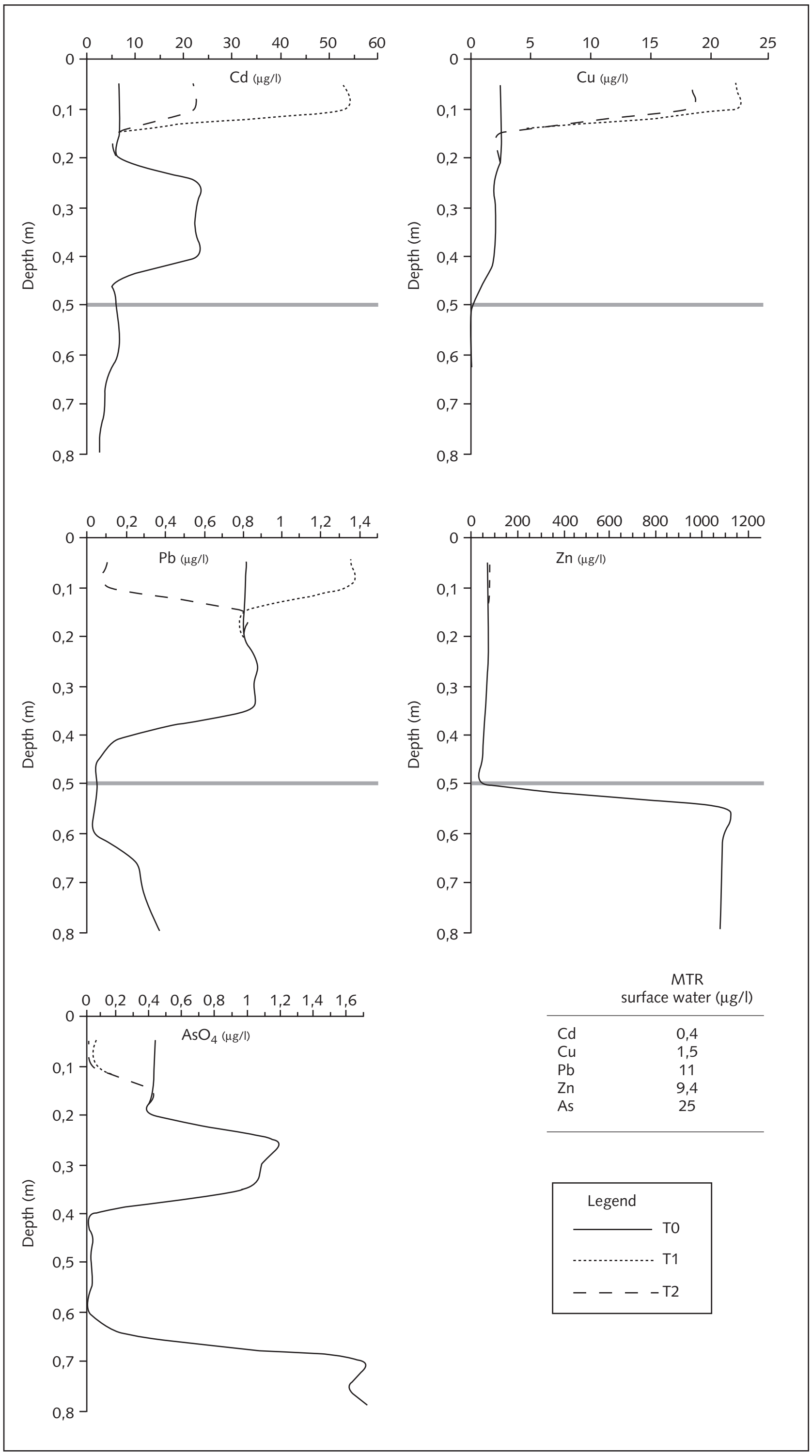


Figure 7
Pore water concentrations for three scenarios after 270 days.
The grey line is the ground water level.

	MTR surface water (µg/l)
Cd	0,4
Cu	1,5
Pb	11
Zn	9,4
As	25

The dissolved organic carbon (DOC) concentration in the pore water of the deposited layer is estimated at 4,8 mg/l. As a starting value for solid organic carbon content (SOC) we chose a value within the same order of magnitude as the SOC in the top layer of the flood plain soil (i.e., 3%).

As is shown in figure 7, the T1 scenario results in an increase of all metal concentrations, except arsenic, in the top 10 cm. The effect is most severe for cadmium and copper (Cd from 6,7 to 53 µg/l; Cu from 2,5 to 22,1 µg/l). The effect on zinc is minor (from 73 to 83 µg/l). Zinc however has its highest dissolved concentrations below the ground water level.

The T2 scenario mainly results in less excessive concentrations in the pore water of the top layer than calculated for the T1 scenario, and even shows a quality improvement for Pb. Zn concentrations are only slightly affected, which was somewhat unexpected regarding the large differences in total content.

It is noteworthy to mention that the bioavailable fractions of Cd and Cu in pore water, however very high, do not proportionally increase with the significant increase in total contents. For example, the cadmium content in the toplayer of the flood plain soil increases by a factor 46 as a result of the T1 scenario. Concentrations in pore water however increase "only" by a factor of 8. For copper, total content increases 59 times, while dissolved concentrations increase 9 times. Since SOC is assumed to be comparable in the three scenarios, the explanation of the less than proportional increase in the pore water concentrations is most presumably found in the high iron content of the Dommel's suspended sediments. Fe-oxides are very effective binding substrates for metals, and may therefore contribute to a larger sorption capacity of the new top layer. To compare old and new situations, the distribution coefficients of the T0, T1 and T2 top layers were calculated by dividing solid-phase bound metals by dissolved concentrations (see table 4). In all cases (except maybe Cd for the third scenario), the new deposited sediment layer has a larger potential for binding metals to the soil matrix (larger values indicate more binding) both for T1 and T2. It is advised however to use these values as indicative entities, e.g. for trend observations rather than absolute values to calculate, for example, mobility.

Table 4
Indicative distribution coefficients Kd (l/kg) of "old" and "new" top layers

	Scenario		
	T0 (present)	**T1**	**T2**
Cd	750	4.400	600
Cu	2.560	19.900	5.800
Pb	82.000	66.500	112.000
Zn	1.650	79.500	30.000
As	552.000	>4.10^6	>4.10^6

4.3 Plant uptake

The underlying mechanisms for the uptake of metals by plants are explained in section 2.2.2. Four plant categories are distinguished: monotocyls (grasses), rhizobium-dicotyls (e.g., clovers), dicotyls (most herbs) and hyperaccumulators (willow). Each category responds differently to different sources of metals. This may be total content in soil and/or dissolved concentrations of free ions.

The rooting zone, i.e. the zone over which metals are available for plant roots, differs for each category. For monocotyls, this zone was set at 5-20 cm. For the other plant categories, this zone was 20-50 cm, corresponding to the average occurrence of the bulk of fine roots. Further, it is assumed that no roots develop below ground water level. Results are shown in figure 8.

As was expected, little effects *between scenarios* are observed. This is solely attributed to the fact that the deposited sediment layer of 10 cm is too small to achieve physical contact between the sediment and the roots of most plants. For monocotyls however, some differences occur. Grasses have a (defined) rooting depth of 5-20 cm, and their roots are therefore exposed to the new sediment layer. As a result, internal contents of the shoots are doubled from 0.15 mg/kg dw in the T0-scenario to 0.31 mg/kg dw in the T1-scenario.
Cadmium and zinc are effectively accumulated by willow. Dicotyls take up copper in larger amounts. It should be noted however that the risks of plant uptake is not so much the toxicity to the plant itself, but its transfer to herbivores, and more generally in terms of biomagnification. Cornelissen (2000) summarized the dietary patterns of 16 different herbivores that inhabit flood plain habitats. The contributions of monocotyles, dicotyles and willow in their total dietary uptake of plants were measured. The actual risk of each metal should therefore be related to the total amount of uptake of each plant category (Table 5).

Figure 8

Concentrations of cadmium, copper, and zinc, in four plant categories for scenario T0, T1 and T2.

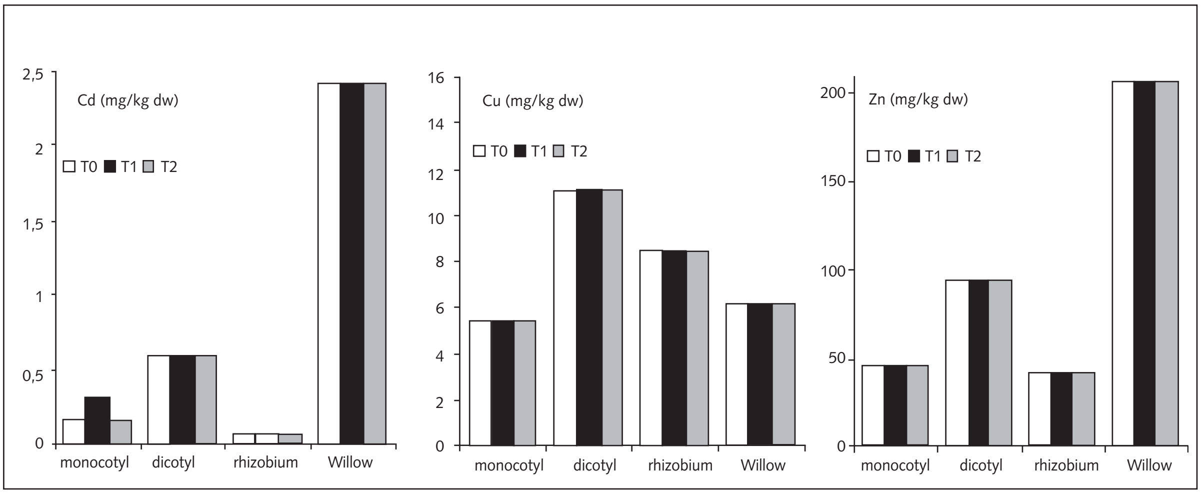


Table 5

Food categories that contribute to the dietary uptake of herbivores. Grey areas are preferred food categories.

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
Aquatic plants	X	X								X			X			
Monocotyls	X	X	X	X	X	X	X	X	X		X	X	X	X	X	X
Dicotyls	X	X	X	X	X	X	X	X	X		X	X	X	X	X	X
Woody dicotyls	X	X	X	X	X	X	X	X		X	X	X	X	X		
Roots		X			X			X	X	X				X		
Fruits/nuts	X	X			X			X	X					X		
Moss/lichen	X	X	X	X	X			X				X		X		
Mushrooms	X	X			X			X	X					X		
Grain	X	X	X	X	X	X	X	X	X		X			X	X	X
Agricultural crops	X	X	X	X	X	X	X	X	X		X	X		X	X	X

1 = cattle, 2 = horse, 3 = sheep, 4 = goat, 5 = pig, 6 = red deer, 7 = roe deer, 8 = wild boar, 9 = badger, 10 = beaver, 11 = hare, 12 = rabbit, 13 = rat, 14 = mouse, 15 = goose, 16 = duck.

Table 5 shows that grasses are, as a food category, preferred by most herbivores, and may therefore impose a significant contribution to the dietary uptake of cadmium. The increased accumulated Cd in scenario T1 by monocotyls is therefore certainly not insignificant. It is apparent that actual risks at the Borkel site depend on the type of land use and habitat, and key species that may occur or are foreseen in future redevelopment situations.

4.4 Accumulation by invertebrates

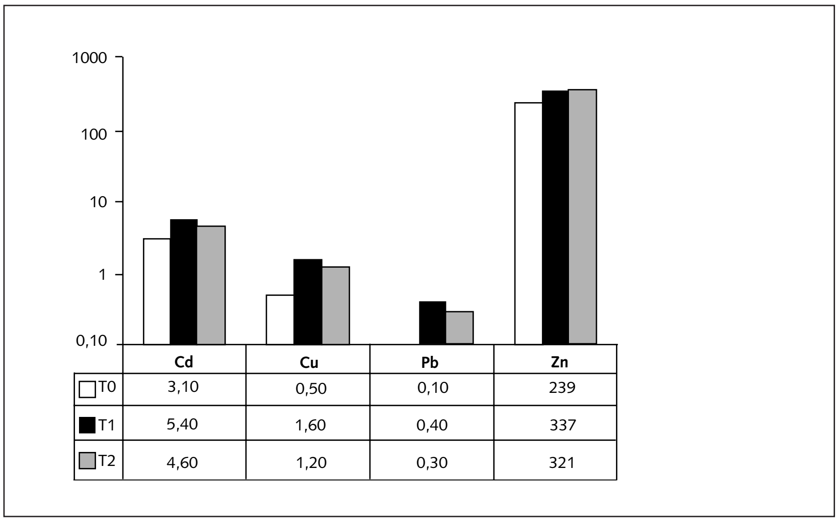
Figures 9 and 10 show the calculated body concentrations of the earthworm *L. rubellus* and the isopod *P. scaber* after 270 days (=3 months after inundation and subsequent sedimentation of the new sediment layer).

It was assumed that the earthworm accumulates its metals over the entire soil layer above the ground water, i.e. 50 cm. In contrast, the isopod collects its metals solely from the top layer, i.e. 10 cm. Sources of metals are soil, pore water and food, which are all included in the transfer functions (section 2.2.3). Food is defined as leaf litter, and the metal content is read directly from the plant module output.

The results show that both T1 and T2 scenarios lead to an increase of body concentrations. The effect is most pronounced for the isopod. As was explained in section 2.2.3, the contribution of soil and food (leaf litter) to the total uptake is much larger for the isopod than for the earthworm, which takes up metals predominantly from the dissolved phase. The effect of the limited contact zone for the isopod is particularly large compared to the earthworm, because the earthworm may experience some "dilution" due to its larger forage zone with lower pore water concentrations.

Figure 9

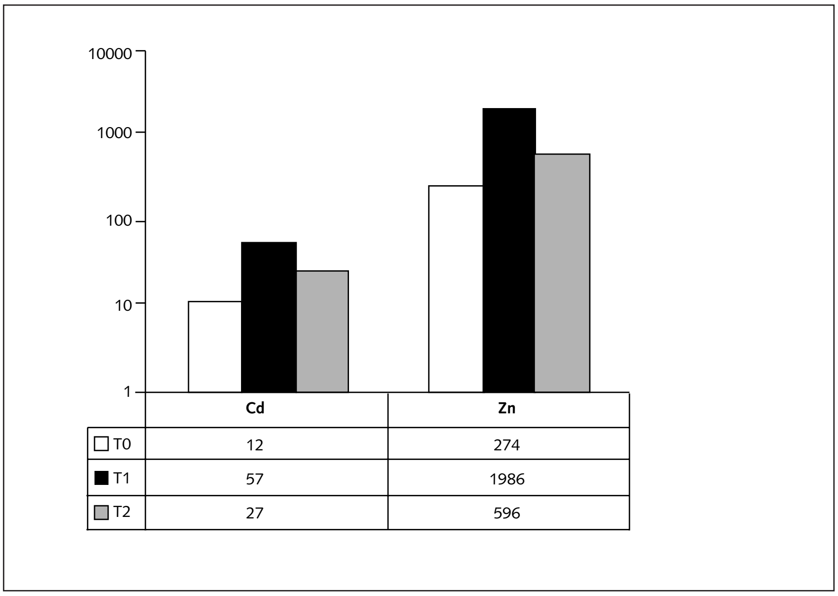
Body concentrations in *Lumbricus rubellus* in three scenarios.



	Cd	Cu	Pb	Zn
□ T0	3,10	0,50	0,10	239
■ T1	5,40	1,60	0,40	337
▨ T2	4,60	1,20	0,30	321

Figure 10

Body concentrations in *Porcelio scaber* in three scenarios.



	Cd	Zn
□ T0	12	274
■ T1	57	1986
▨ T2	27	596

The results show that the largest body concentrations for these invertebrates will occur with scenario T1. Metal accumulation is a factor 2 (Cd, worm) to 7 (Zn, isopod) larger than in the present T0 situation. For the T2 scenario, body concentrations are lower than for the T1 scenario, but are still elevated in comparison to the present T0 situation.

It is again noted that the calculated values should be interpreted in a qualitative manner.

5. Conclusions

Based on the on-site measurements and the simulation of three scenarios with BioChem-DSS, the following conclusions are drawn:

- In the present T0 situation, metal concentrations decrease with depth, showing in most cases their peak concentration in the 20-40 cm below surface layer. Arsenic and cadmium exceed MTR quality standards.

- The quality of the suspended solids from the Dommel is very poor. As, Cd, Cu, Ni, Pb, Zn concentrations all exceed MTR values, and in almost all cases the Intervention value is exceeded by some factors. Of most concern are the concentrations of Cd and Zn. These metals exceed Intervention values by a factor of 20 and 7, respectively.

- A sedimentation layer of 10 cm is for most plant groups insufficient to influence the uptake of metals to shoots. For monocotyls (grasses) however, some differences occur. Compared to the present T0 situation, internal contents of cadmium in the shoots are doubled in the T1 scenario. As a food category, grasses are preferred by most herbivores, and may therefore impose a significant contribution to the dietary uptake of cadmium.

- For invertebrates, the largest body concentrations will occur with scenario T1. Metal accumulation is a factor 2 (Cd, worm) to 7 (Zn, isopod) larger than in the present T0 situation. For the T2 scenario, body concentrations are lower than for the T1 scenario, but are still elevated in comparison to the present T0 situation.

- Measures to decrease the metal load in Eindergatloop, discharging into the Dommel, may in an ecotoxicological sense be well effective. The quality of the suspended matter in the Dommel will improve. Sedimentation however will still lead to elevated risks, compared to the present situation. These risks then depend on the type of land use and habitat, and on the key species that may occur or are foreseen in future redevelopment situations.

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Appendix

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BIOCHEM column definition T0

        version 2.0 - 2006      DOMMEL 2004007 (X=159350; Y=367770)
. . . . . . . . . . . . . .interface properties. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . .
Var:  x         avg_DOC   SOC     Al.soil.sum     PO4.soil.sumFe.soil.sum    Cd.soil.sum  Cu.soil.sum  Zn.soil.sum  Pb.soil.sum   AsO4.tot.sumMn.soil.sum   clay_content  SO4.soil.sum avg_H.act
Data:   -0.10    2.72E-05     0.1       0.52            0.028          0.5             2.46E-05     1.38E-03     8.02E-03    1.11E-03     5.00E-01      1.40E-02      0.136         1.00E-02     3.80E-08
Data:   -0.05    2.72E-05     0.1       0.52            0.028          0.5             2.46E-05     1.38E-03     8.02E-03    1.11E-03     5.00E-01      1.40E-02      0.136         1.00E-02     3.80E-08
. . . . . . . . . . . . . .column properties. . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . . .
Var:    x   DOC       SOC       Al.soil.sum  PO4.soil.sumFe.soil.sum     Cd.soil.sum Cu.soil.sum  Zn.soil.sum   Pb.soil.sum AsO4.tot.sumMn.soil.sum clay_content SO4.soil.sum H.act
        [m]             [kg/l]      [kg/kg]    [mol/kg]   [mol/kg]   [mol/kg]   [mol/kg]   [mol/kg]   [mol/kg]   [mol/kg]   [mol/m3] [mol/kg]  [kg/kg]     [mol/l]
Data:     1.00E-80   4.80E-06   2.60E-02   9.60E-01   2.00E-02   1.20E-01   4.61E-05     1.21E-04    1.38E-03    3.25E-04    7.128E-01   4.39E-03    1.34E-01   1.34E-03    3.89E-08
Data:     5.00E-02   4.80E-06   2.60E-02   9.60E-01   2.00E-02   1.20E-01   4.61E-05     1.21E-04    1.38E-03    3.25E-04    7.128E-01   4.39E-03    1.34E-01   1.34E-03    3.89E-08
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Data:     2.00E-01   4.80E-06   2.60E-02   9.60E-01   2.00E-02   1.20E-01   4.61E-05     1.21E-04    1.38E-03    3.25E-04    7.128E-01   4.39E-03    1.34E-01   1.34E-03    3.89E-08
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Data:     3.00E-01   2.72E-06   3.50E-02   1.020000   2.00E-02   2.11E-01   14.09E-05    1.30E-04    2.64E-03    3.56E-04    16.8E-01    2.28E-03    2.02E-01   1.34E-03    3.89E-08
Data:     3.50E-01   2.72E-06   3.50E-02   1.020000   2.00E-02   2.11E-01   14.09E-05    1.30E-04    2.64E-03    3.56E-04    16.8E-01    2.28E-03    2.02E-01   1.34E-03    3.89E-08
Data:     4.00E-01   2.72E-06   3.50E-02   1.020000   2.00E-02   2.11E-01   14.09E-05    1.30E-04    2.64E-03    3.56E-04    16.8E-01    2.28E-03    2.02E-01   1.34E-03    3.89E-08
Data:     4.50E-01   2.72E-06   3.10E-02   1.180000   2.00E-02   2.68E-01   5.35E-05     6.60E-05    5.96E-03    8.98E-05    16.8E-01    1.73E-03    1.59E-01   1.34E-03    3.89E-08
Data:     5.00E-01   2.72E-06   3.10E-02   1.180000   2.00E-02   2.68E-01   5.35E-05     6.60E-05    5.96E-03    8.98E-05    11.6E-01    1.73E-03    1.59E-01   1.34E-03    3.89E-08
Data:     5.50E-01   2.72E-06   3.10E-02   1.180000   2.00E-02   2.68E-01   5.35E-05     6.60E-05    5.96E-03    8.98E-05    11.6E-01    1.73E-03    1.59E-01   1.34E-03    3.89E-08
Data:     6.00E-01   1.60E-06   3.10E-02   1.180000   2.00E-02   2.68E-01   5.35E-05     6.60E-05    5.96E-03    8.98E-05    0.274000    1.73E-03    1.59E-01   1.34E-03    3.89E-08
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Data:     7.00E-01   1.60E-06   2.20E-02   1.600000   2.00E-02   3.30E-02   2.85E-05     8.50E-05    4.67E-03    6.84E-05    0.274000    1.22E-03    1.34E-01   8.48E-04    3.89E-08
Data:     7.50E-01   1.60E-06   2.20E-02   1.600000   2.00E-02   3.30E-02   2.85E-05     8.50E-05    4.67E-03    6.84E-05    0.274000    1.22E-03    1.34E-01   8.48E-04    3.89E-08
Data:     8.00E-01   1.60E-06   2.20E-02   1.600000   2.00E-02   3.30E-02   2.85E-05     8.50E-05    4.67E-03    6.84E-05    0.274000    1.22E-03    1.34E-01   8.48E-04    3.89E-08
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Data:     9.00E-01   1.60E-06   2.20E-02   1.600000   2.00E-02   3.30E-02   2.85E-05     8.50E-05    4.67E-03    6.84E-05    0.274000    1.22E-03    1.34E-01   8.48E-04    3.89E-08
Data:     9.50E-01   1.60E-06   2.20E-02   1.600000   2.00E-02   3.30E-02   2.85E-05     8.50E-05    4.67E-03    6.84E-05    0.274000    1.22E-03    1.34E-01   8.48E-04    3.89E-08
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