

BIOCHEM—ORCHESTRA: A tool for evaluating chemical speciation and ecotoxicological impacts of heavy metals on river flood plain systems

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A diagnostic risk-assessment tool for heavy metals, based on biotic and abiotic interactions, compares risks under different environmental scenarios.

Abstract

The chemical speciation model BIOCHEM was extended with ecotoxicological transfer functions for uptake of metals (As, Cd, Cu, Ni, Pb, and Zn) by plants and soil invertebrates. It was coupled to the object-oriented framework ORCHESTRA to achieve a flexible and dynamic decision support system (DSS) to analyse natural or anthropogenic changes that occur in river systems. The DSS uses the chemical characteristics of soils and sediments as input, and calculates speciation and subsequent uptake by biota at various scenarios. Biotic transfer functions were field-validated, and actual hydrological conditions were derived from long-term monitoring data. The DSS was tested for several scenarios that occur in the Meuse catchment areas, such as flooding and sedimentation of riverine sediments on flood plains. Risks are expressed in terms of changes in chemical mobility, and uptake by flood plain key species (flora and fauna).

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1. Introduction

The uptake of heavy metals by biota in the environment is governed by a combination of chemical, physical and biological processes. To fully understand and predict the impact of heavy metals on biota, mediated by environmental conditions, mechanistic modelling has become a necessity. Reliable risk assessment nowadays comprises the fields of chemistry, ecotoxicology, and physical sciences such as hydraulics. Increasing insight into the factors that define environmental risks has made the prediction of risks a matter of complex interactions between these fields.

Over the past years, some interesting models have become available for risk assessment. The common denominator of these models is that they are increasingly based on actual mechanisms (chemical and/or biological) rather than on empirical relationships, and that they therefore potentially have better predictive capabilities. Examples are the development of biotic ligand models (BLM; e.g. Warren et al., 1998; Paquin et al., 2002; Niyogi and Wood, 2004; Kola and Wilkinson, 2005), which make an effort to combine chemical speciation and uptake kinetics, and mechanistic models (e.g. Simpson and King, 2005; Hendriks et al., 1995, 2006) that aim to assess generic risks for policy purposes. Generally, these tools are limited in predicting the impact of physical changes – the environment – on chemical speciation and, consequently, uptake by biota. Very few models are available to analyse the

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effects of changing hydrological conditions on soils and sediment, which may result in alterations of the redox regime. For flood plain soils that are periodically inundated, or soil or sediment that is moved, buried, flooded, or irrigated, redox-mediated processes are of decisive importance, as these processes have a large impact on soil chemistry and element mobility. It is therefore essential to sufficiently understand the mechanisms that dictate the overall abiotic and biotic effects.

For this purpose, a decision support system (DSS) has been developed that takes these effects into account. It is designed to evaluate and compare scenarios with metal-containing sediments under various environmental conditions. This paper presents the DSS by describing its structural and functional designs, and shows briefly the outcome of some scenario exercises in order to show possibilities for application.

2. Methods

2.1. Structural design

The decision support system BIOCHEM consists of a collection of separate modules, described below, that handle different processes involved in the uptake of elements by organisms, and was implemented within the ORCHESTRA modelling framework (Meeussen, 2003). Within this framework, models can be set up in terms of (spatial) cells, that represent parts of a model system (e.g. a layer of soil, organisms, plant root, etc.), connections between cells with user-defined functions (e.g. mass transport by diffusion, convection, or organism uptake functions) that operate on pairs of cells, and functions that operate on individual cells (e.g. chemical equilibrium module that calculates chemical equilibrium for a cell).

The main role of ORCHESTRA is to act as a calculating platform to solve the BIOCHEM equations. The complete definition of BIOCHEM, in terms of formulas, equations, variables, etc. is present in ORCHESTRA input files. A unique property of the ORCHESTRA framework is that all these function modules are fully user-definable, in an object-oriented structure in text format, and used as input during a model run. In fact, the ORCHESTRA calculation kernel (Java source code) does not contain any model equations. All BIOCHEM model equations are thus read from text files, which make it possible to change or extend the DSS without recompiling the ORCHESTRA source code.

The ORCHESTRA framework contains an extensive standard object library for advanced chemical speciation models that can be used as building blocks for new models. This structure makes it possible to implement a DSS that contains a sophisticated chemical speciation module. The user-defined uptake models can make use of information on the chemical conditions as a function of depth that is generated by the chemical equilibrium module. The main parameter that is used in the BIOCHEM uptake model is the dissolved element concentration.

In BIOCHEM Version 2.0 (Vink and Schröder, 2006), spatial cells are defined that represent a soil column of 1 m depth. Each of these cells contains a set of variables that defines the local chemical, physical and biological compositions of this soil compartment. During the calculations, the different modules are called in succession per time step. First, the initial hydrology and chemistry of the cells are read from an input file; then, the chemical speciation in each cell is calculated per time step, and subsequently mass transfer between cells and between different compartments (including biota) is calculated.

2.2. Functional design

BIOCHEM consists of a chemical module, a plant module, and an invertebrate module. These will be explained in the following paragraphs.

2.2.1. Chemical module

BIOCHEM is built around a soil chemical model that calculates the solid–solution partitioning and speciation of heavy metals in soils (Schröder and Vink, 2004; Schröder et al., 2005; Schröder, 2005). It includes the chemical processes as described in CHARON+ (De Rooij and Kroot, 1991; Vink et al., 1999). Solid–solution partitioning is calculated by combining models for adsorption by clay and iron oxide surfaces (CD-MUSIC; Hiemstra and Van Riemsdijk, 1996). Sorption to manganese oxide surfaces is described by a surface complexation model of Tonkin et al. (2004). Equilibrium constants for soluble species and mineral phases were used from MINTEQ2 (Allison et al., 1991) recent database Version 4.0. The activity of Fe^{3+} is controlled by the presence of goethite, and the activity of Al^{3+} is governed by gibbsite. Adsorption to the solid phase and dissolved organic matter (DOM) is calculated using a multisurface approach. We used the consistent non-ideal competitive adsorption model NICA that uses a Donnan approach to describe electrostatic interactions (Benedetti et al., 1995; Kinniburgh et al., 1996).

The chemical module includes all minerals that are likely to occur in flood plain sediments. It uses total element concentrations per cell as input (Al, As, Cd, Cu, Fe, Mn, P, Pb, SO_4 , and Zn). The amounts of iron oxides and manganese oxides are coupled to the adjacent mineral phases and are therefore calculated automatically by the system. The module calculates partitioning of elements over all different chemical forms including distribution over aqueous and solid phases as output. BIOCHEM is field-validated with a large number of abiotic and biotic samples and one-site pore water measurements (Cornelissen, 2002; Bernhard et al., 2005; Schröder et al., 2005; Schröder, 2001, 2005).

2.2.1.1. Soil moisture content. BIOCHEM makes use of a flexible algorithm for the distribution of water in the soil column. Generally, the porosity is not critical and therefore fixed to a value of 0.5 (1/l). In the saturated layers, θ_g (gas volume) is constant and only present at a low value ($1\text{E}-6$) for numerical reasons. At the surface, θ_w (water volume) is set to a minimum value of $1\text{E}-6$. In the unsaturated layers, the water saturation is described by a gamma function.

θ_w is calculated by

$$\theta_w = \begin{cases} \text{porosity} - \min_{\text{gas}} & x \geq \text{water level} \\ dx_{w2} (\text{porosity} - \min_{\text{water}}) + \min_{\text{water}} - \min_{\text{gas}} & x < \text{water level} \end{cases}$$

and θ_g is

$$\theta_g = \text{porosity} - \theta_w$$

with

$$dx_{w1} = \begin{cases} x/\text{water level} & \text{water level} \leq 0 \\ 1 & \text{water level} > 0 \end{cases}$$

and

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

2.2.1.2. Water level. The water level is read from a separate input file consisting of 365 values representing the daily water level relative to the surface. By using values explicitly defined in the input file, BIOCHEM can make use of real-time measurements, hydrological model predictions or interpolation of data from the Dutch National DONAR database (Donar, Internet) and Excel applications. 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 level measured in the river Rhine over an 18-year period (1985–2003). The data are converted to a water level in a given flood plain, its location indicated by river kilometer according to the Dutch river indication system.

2.2.1.3. Redox potential. The redox potential is related to the water level and the algorithm to calculate this 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 measure field data;
- above the groundwater table, the rate of decrease will depend on the groundwater table; and
- 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:

$$\Delta pe = \begin{cases} \text{pH} + 6 - 8 \times dx_{w1}^{\gamma} & x < \text{water level} \\ 12e^{-\alpha(x-\text{water level})} - \text{pH} & x \geq \text{water level} \end{cases}$$

with

$$dx_{w1} = \begin{cases} x/\text{water level} & \text{water level} > 0 \\ 0 & \text{water level} \leq 0 \end{cases}$$

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 at a given time t 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 via root respiration (see below). 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.

2.2.1.4. Oxidation processes. BIOCHEM contains two modules to represent oxidation processes. The first, *C_conversion*, contains a general oxidation term comparable to the approach followed in CHARON+. With the second module *Roots* a similar process can be applied to a limited layer, the root zone. Both modules offer the flexibility to define different formulae 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 pCO₂ by simple algorithms.

2.2.1.5. Diffusion. The modules Diffusion and Gas_diffusion define the diffusion processes in the water phase. In principle, 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. In the current version of BIOCHEM we make use of

$$J_{\text{gas diffusion}} = -4D_g dC_g \theta_g^{3.1}$$

2.2.2. Plant module

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

- define the relevant root zone for a flood plain;
- define a time-dependent uptake behaviour; and
- calculate metal uptake in time.

The plant module is field-validated, and algorithms are of empirical kind. We used the measurements of metal contents in 16 plant species, in 42 flood plains of eight river systems over a period of two years (Schröder, 2001; Cornelissen, 2002) to derive these algorithms. Statistical clustering (Cornelissen, 2002) yielded four plant categories:

1. monocotyls;
2. non-rhizobium forming dicotyls;
3. rhizobium forming dicotyls; and
4. willows (active accumulator).

Schröder (2005) summarized the regression coefficients for the metal uptake in the four plant categories. For all categories, significant regressions could be fitted for Cd ($p < 0.05$), Cu ($p < 0.1$), and Zn ($p < 0.1$). Differences between seasons were observed, but a seasonal correction in the transfer functions did not improve the standard error or the significance of the regression parameters.

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

$$\text{Cd}_{\text{willow}} (\text{mg kg}^{-1}) = 2.36 + 1.847 \times 10^6 \times \text{average}_{\text{Cd}}$$

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

$$\text{average}_{\text{Cd}}(t) = \sum_{\text{nodes}, t} \frac{\text{Cd} \cdot \text{water} \cdot \text{sum}(\text{node}, t)}{\text{nodes} \times t}$$

where *nodes* represents the number of soil layers, and Cd·water·sum is the total dissolved Cd concentration in pore water. 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. Root zone layer thickness can be changed accordingly.

2.2.3. Invertebrates module

To link metal speciation to bioaccumulation in invertebrates, 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 compartmentalisation. 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 uptake) 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 to biota is given. For details we refer to Vijver (2005).

2.2.3.1. Soft-bodied species. For earthworms and related species, uptake and elimination can be described with a two-compartment model with first order kinetics (Vink, 2002, 2005; Vijver et al., 2005). During exposure of earthworms to a polluted soil, accumulation in time ($Cw(t)$ in $\mu\text{g/g}$) can be estimated according to Eq. (1) describing the first compartment and Eq. (2) describing the second compartment of the bioaccumulation:

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

$$Cw(t) = \frac{k_i a}{(k_2 + k_i)^2} [(k_2 + k_i)t + e^{-(k_2+k_i)t} - 1] \quad (2)$$

in which k_2 is the elimination rate constant (d^{-1}), k_i 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 ($=k_1 \times$ external metal concentration) divided into two fluxes either via the dermal (d) or oral (o) route, defined as:

$$a = k_1 d [\text{Me}]_t + k_1 o [\text{Me}]_x \quad (3)$$

in which the first metal species $[\text{Me}]_t$ is representing the total pore water metal concentration ($\mu\text{g L}^{-1}$). The second metal species $[\text{Me}]_x$ represents metals

bound to inorganic and organic ligands and bound to organic matter and 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 HNO₃ extraction. The fraction of metal taken up via the dermal route is denoted as 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 routes and can be used as a check on the calculation of metal bioaccumulation in earthworms.

2.2.3.2. Hard-bodied species. For organisms having a firm exoskeleton, uptake and elimination can be described as (Vijver et al., 2006):

$$Ci(t) = \frac{a}{k_2} [1 - e^{-k_2 t}] [F_i + (1 - F_i)e^{-k_2(t)}] \quad (4)$$

in which k_2 is the elimination rate constant (d^{-1}), t is time per day. F_i is the fraction (ranging from 0 to 1) that cannot be eliminated and is stored in the body. The variable a is the uptake rate flux, divided into a pool of metals taken up via soil and a pool taken up via food. Metal accumulation by isopods is 50% from soil and 50% from food intake (Vijver et al., 2006):

$$a = k_{1s}[Me]_s + k_{1f}[Me]_f \quad (5)$$

where k_{1s} is the uptake rate constant from the soil (in $g\ g_{\text{animal}}^{-1}\ day^{-1}$) and k_{1f} is the uptake rate constant from the food (in $g\ g_{\text{animal}}^{-1}\ day^{-1}$). The metal species $[Me]_s$ 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) as the food source.

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, and 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).

Fig. 1 shows the interactive processing routings of the above-described modules.

2.3. Case study: Meuse tributary Dommel

Many scenario analyses have been performed with BIOCHEM-DSS, including the variations of flooding events and groundwater shifts along a 150 km transect of the river Meuse. Here, we choose to present a case study that was performed for the river Dommel, a tributary to the river Meuse, since this study required all modules and functionalities of BIOCHEM-DSS, and is therefore representative for its range of application. The study was performed within the EU-KP6 Programme AquaTerra (2005) sub-programme BASIN-Meuse.

The Dommel catchment area struggles with some environmental issues concerning the large-scale contamination of heavy metals, mainly Zn and Cd. Besides emissions of nutrients from agricultural sources, historical pollution of heavy metals from zinc factories is one of the main problems in this region. A number of measures have or will be taken in the near future to create a higher water retention volume in the upstream Dommel catchment during high discharge periods. These measures are related to redevelopment projects in the Meuse river, which may lead to a (temporarily) hampered discharge of the Dommel into the Meuse. Among these measures is the assignment of retention areas for water storage (Joziassse et al., 2005). Therefore, a reliable

prediction of water quality and transported sediment is necessary. This determines the loading of flooded areas with contaminated suspended material that remains on the flood plain soil after settling. Another possible measure is the sanitation of the river Eindergatloop, which is responsible for up to 80% of the contaminant load in the Dommel.

One of the intended storage areas is the nature reserve area Malpie. Detailed and representative data of the composition of an 80-cm soil layer were collected ($X = 159\ 350$; $Y = 367\ 770$; $pH = 7.32$, $SO_4 = 128.9\ mg\ L^{-1}$). Also, the composition of suspended solids was determined via centrifugation of surface water in the adjacent Dommel and before the discharge point of Eindergatloop.

Three scenarios were defined:

- Scenario T0: present situation of metal availability in the flood plain soil;
- Scenario T1: sedimentation of 10 cm of sediment from the Dommel onto the floodplain soil; and
- Scenario T2: sanitation of Eindergatloop, resulting in zero emission of metals into the Dommel.

Water balance and the water level movement are kept uniform for all three scenarios. In order to simulate actual inundation and sedimentation, the water level is maintained at +0.2 m for a period of six months, in order to reach thermodynamic steady state conditions, followed by descent of the water level to -0.5 m, which represents the average present situation.

3. Results

Table 1 shows that the composition of the soil – a clayey fluvisol – varies considerably with depth. Contaminant concentrations decrease with depth, showing in most cases their peak concentration in the 20–40 cm layer. Tables 2 and 3 show the composition of the suspended solids, respectively, prior and after sanitation of Eindergatloop (i.e. Dommel upstream sampling point).

The present quality of the suspended solids in the Dommel is very poor. As, Cd, Cu, Ni, Pb, and Zn concentrations all exceed quality standards (MTR), and in all cases the upper quality standard (Dutch Intervention value) is exceeded by some factors, most for Cd and Zn (factors 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 (e.g. Sonke et al., 2002). Additional concern is the eutrophic state of the surface water, illustrated by a high P content.

BIOCHEM is able to calculate time-dynamic speciation for all elements, including arsenic. For this case study, we only present results for Cd and Zn. Fig. 2 shows the dynamic speciation calculation for the flood plain soil. The shown 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 recognized in the graph's shapes.

The effect of the hydraulic movement is directly expressed in the chemical speciation. Oxidation of the soil leads to shifts in mineral composition, and especially sulfides, iron oxyhydroxides and manganese oxides undergo major changes. As a result, sorption and complexation of metals and arsenic to soil components are affected. Results for arsenic showed that an

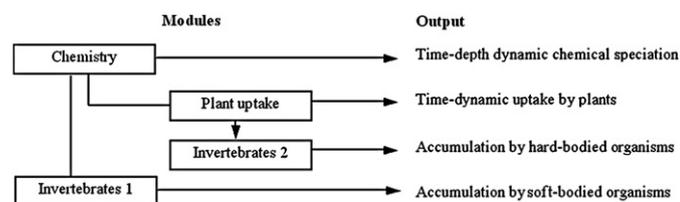


Fig. 1. Processing route.

Table 1

Soil characteristics of the flood plain soil

| Depth (cm) | <2 μm (%) | Tot C (%) | All (g kg ⁻¹) | Mn (g kg ⁻¹) | Fe (g kg ⁻¹) | P (g kg ⁻¹) | Ca (g kg ⁻¹) | Cr (mg kg ⁻¹) | Ni (mg kg ⁻¹) | Cu (mg kg ⁻¹) | Zn (mg kg ⁻¹) | As (mg kg ⁻¹) | Mo (mg kg ⁻¹) | Cd (mg kg ⁻¹) | Pb (mg kg ⁻¹) |
|------------|----------------------|-----------|---------------------------|--------------------------|--------------------------|-------------------------|--------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| 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 | 15.80 | 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 |

inundation period of three months is the maximum time length to prevent MTR quality standards to exceed (data not shown).

T1 and T2 scenarios 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 Fig. 3. Zinc is governed mainly by ZnFe₂O₄. 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 of the top layer of the flood plain soil (i.e. 3%). It is assumed that Cd that is associated to suspended material is reversibly bound (Comans and Van Dijk, 1988).

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 $\mu\text{g/l}$; Cu from 2.5 to 22.1 $\mu\text{g/l}$). The effect on zinc is minor (from 73 to 83 $\mu\text{g/l}$). Zinc, however, has its highest dissolved concentrations below the groundwater 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, are very high, do not *proportionally* increase with the significant increase in total contents. For example, the cadmium content in the top layer 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 nine times (data not shown). Organic carbon contents of suspended matter and soil are comparable. The explanation was found in the high iron content of Dommel’s suspended sediments. Fe-oxides are very effective binding substrates for metals, and therefore contribute to a larger sorption capacity of the new top layer, which was underpinned by the dominant calculated Cu-solid phase.

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 (Table 4). Generally, the new deposited sediment layer has a larger potential for binding metals to the soil matrix, both for T1 and T2 scenarios. 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.

Results for uptake by plants are shown in Fig. 4. The rooting zone, i.e. the zone over which metals are available for plant roots, differed for each plant 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 groundwater level.

Differences between plant categories are large but, 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 thin 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⁻¹ dw in the T0 scenario to 0.31 mg kg⁻¹ dw in the T1 scenario. Cadmium and zinc are effectively accumulated by willow. Dicotyls take up copper in larger amounts (data not shown). 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 monocotyls, dicotyls 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. For example: 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 T1 scenario by monocotyls is therefore certainly not insignificant. It is apparent that actual risks at

Table 2

Suspended matter composition of the Dommel (T1 scenario)

| Susp. solids (%) | <2 μm (%) | Tot C (%) | Al (g kg ⁻¹) | Mn (g kg ⁻¹) | Fe (g kg ⁻¹) | P (g kg ⁻¹) | Ca (g kg ⁻¹) | Cr (mg kg ⁻¹) | Ni (mg kg ⁻¹) | Cu (mg kg ⁻¹) | Zn (mg kg ⁻¹) | As (mg kg ⁻¹) | Mo (mg kg ⁻¹) | Cd (mg kg ⁻¹) | Pb (mg kg ⁻¹) |
|------------------|----------------------|-----------|--------------------------|--------------------------|--------------------------|-------------------------|--------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| | 13.8 | 3.50 | 26.0 | 0.490 | 105.8 | 17.6 | 22.3 | 134.6 | 306.6 | 457.2 | 5171 | 251 | 14.9 | 237.8 | 930.6 |

Table 3
Suspended matter composition of the Dommel after sanitation (T2 scenario)

| Susp. solids (%) | <2 μm (%) | Tot C (g kg ⁻¹) | Al (g kg ⁻¹) | Mn (g kg ⁻¹) | Fe (g kg ⁻¹) | P (g kg ⁻¹) | Ca (g kg ⁻¹) | Cr (mg kg ⁻¹) | Ni (mg kg ⁻¹) | Cu (mg kg ⁻¹) | Zn (mg kg ⁻¹) | As (mg kg ⁻¹) | Mo (mg kg ⁻¹) | Cd (mg kg ⁻¹) | Pb (mg kg ⁻¹) |
|------------------|-----------|-----------------------------|--------------------------|--------------------------|--------------------------|-------------------------|--------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|---------------------------|
| 31.0 | 3.50 | 26.0 | 0.464 | 147.1 | 13.8 | 9.0 | 61.0 | 126.0 | 104.0 | 1783 | 200 | 5.0 | 13.0 | 112.0 | |

the case study site depend on the type of land use and habitat, and key species that may occur or are foreseen in future redevelopment situations.

Fig. 5 shows the calculated body concentrations of the earthworm *Lumbricus rubellus* and the isopod *Porcellio scaber* after 270 days (=90 days 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 groundwater, in this case 0.5 m. In contrast, the isopod collects its metals solely from the top layer, i.e. 0.1 m. Sources of metals are soil, pore water and food,

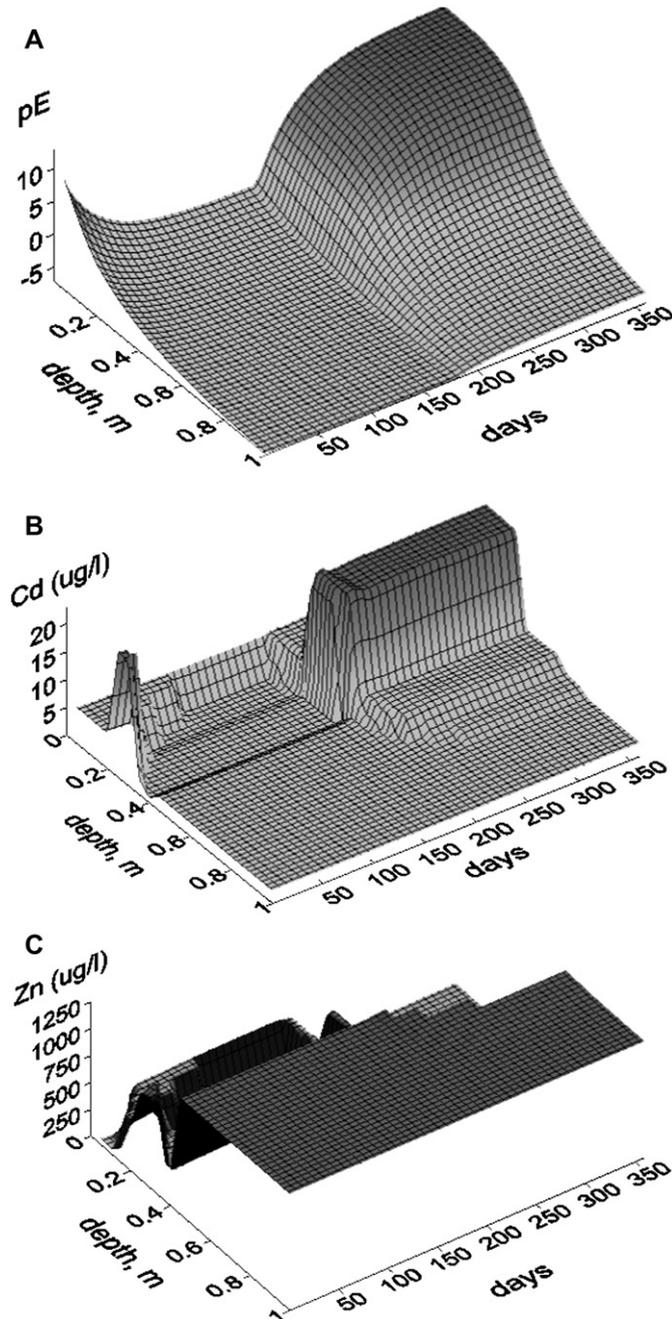


Fig. 2. Time–depth presentations (T0 scenario).

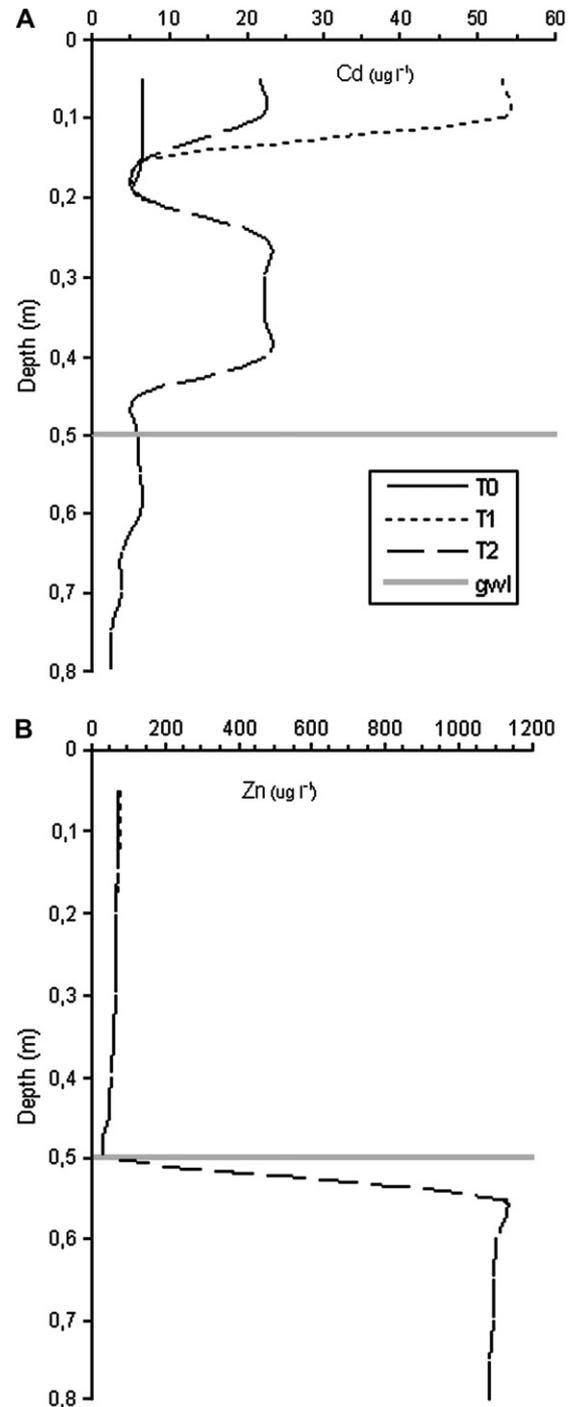


Fig. 3. Cd and Zn concentration profiles in three scenarios. The grey line is the groundwater level at 90 days after inundation.

Table 4
Distribution coefficients K_d ($L \cdot kg^{-1}$) of the sediment's top 10 cm in three scenarios

| | Scenario | | |
|----|--------------|-----------------|-----------------|
| | T0 (present) | T1 | T2 |
| Cd | 750 | 4400 | 600 |
| Cu | 2560 | 19 900 | 5800 |
| Pb | 82 000 | 66 500 | 112 000 |
| Zn | 1650 | 79 500 | 30 000 |
| As | 552 000 | $>4 \cdot 10^6$ | $>4 \cdot 10^6$ |

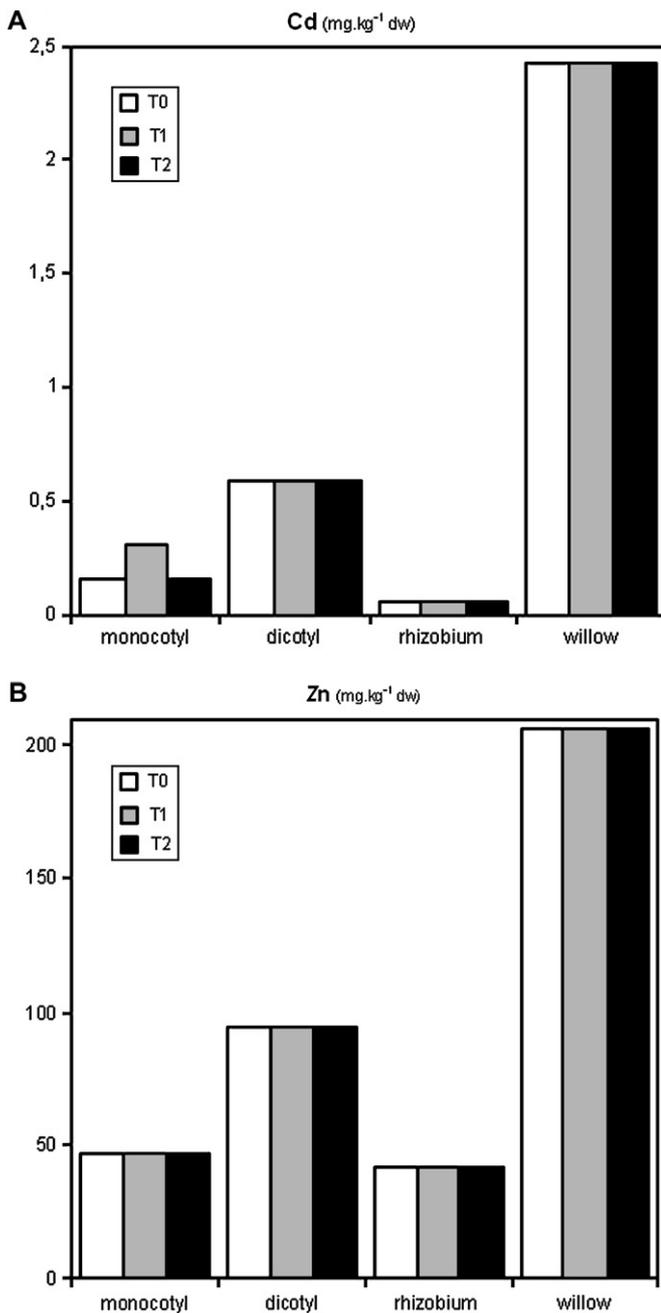


Fig. 4. Cd and Zn concentrations in four plant categories in three scenarios.

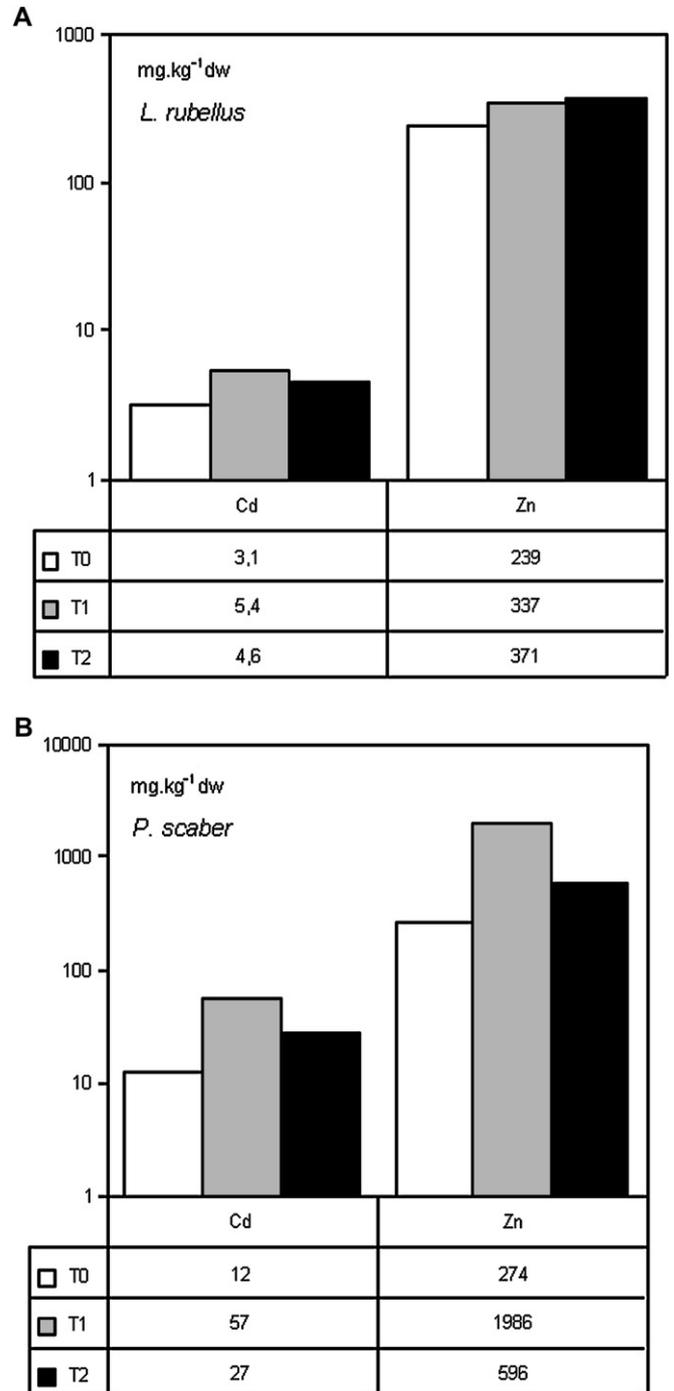


Fig. 5. Cd and Zn body concentrations in *Lumbricus rubellus* and *Porcellio scaber* (log scale) in three scenarios.

which are all adapted 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 for both species. 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 superimposed, because the earthworm experiences some “dilution” due to its larger forage zone with lower pore water concentrations. The largest body concentrations for these invertebrates will occur with T1 scenario. 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.

4. Conclusions

The BIOCHEM-DSS contains a unique combination of advanced chemical, physical, and biological process models. Due to the object-oriented structure of the ORCHESTRA framework, in which it is implemented, BIOCHEM can easily be modified and extended. The DSS provides an interactive, time-dynamic assessment of the chemical behaviour, and biological risks, of heavy metals in river systems.

The simulation of three scenarios for the Dommel–Meuse catchment gave the following conclusions: measures to decrease the metal load of 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. For invertebrates, the largest body concentrations will occur with T1 scenario. 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. These risks then depend on the type of land use and habitat, and key species that may occur or are foreseen in future redevelopment situations.

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