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# Dynamics of metal availability and toxicity in historically polluted floodplain sediments

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## ABSTRACT

Many floodplains contain high concentrations of sediment associated contaminants that might be subjected to large changes in terms of mobility, transformation and bioavailability. Therefore, this study describes 1) changes in the redox conditions and the mobility of metals in artificially uncovered polluted floodplain sediments, 2) metal uptake by organisms and 3) colonization, succession and functioning of benthic algae on these sediments. Flooding caused long term changes in redox potential (Eh) profiles. In top layers strong gradients in redox potential established quickly, while in deeper layers changes occurred more gradually. The availability of copper as measured by Diffusive Gradients in Thinfilms (DGT) showed a consistent relationship with fluctuations in Eh. However, this relationship was restricted to deeper layers in the sediment. Within 1 week high amounts of total copper were immobilized. Differences in total copper concentrations between polluted and clean sediments became only partially apparent when comparing the available copper fraction (DGT-Cu). Introduced *Tubifex* shows only marginal differences in levels of accumulated Cu. Colonization, growth and succession of algal communities on polluted sediments was not impaired, most likely due to low bioavailability. It is concluded that changing environmental conditions, such as flooding, can result in stable chemical conditions with low a availability of metals and hence in a diminution of actual ecological risks.

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## 1. Introduction

Restoration of riverine floodplains alongside the regulated large European rivers can play an important role in the management of floods by reduction of peak discharges and increase of water storage capacity. Proposed measures include setting back dikes, lowering or removing groynes and embankments, extracting accumulated sediments from the floodplains and excavation of secondary channels in the floodplain (Buijse et al., 2002). However, these measures might also have negative consequences because many floodplains contain high concentrations of sediment associated contaminants. Overbank sedimentation and disposal of dredged sediments resulted in increased concentrations of heavy

metals, PACs and other organic toxicants in floodplain soils and sediments (Middelkoop, 2000; Gocht et al., 2001; Winter et al., 2001) that might induce toxic effects (De Haas et al., 2002).

Newly constructed side-channels that are foreseen as means to re-naturalize floodplains will have banks that cut through the aged polluted sediments that have in the meantime been covered by cleaner sediment. The banks of these newly created river channels are characterized by a highly dynamic transition zone (Simons et al., 2001), in which toxicants might be subjected to large changes in terms of mobility, transformation and bioavailability (Van den Berg et al., 1999). On a large scale, differences may be observed between erosion and sedimentation areas and between areas

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with different flooding regimes (Chapman and Wang, 2001). On a smaller scale, changes in the physico-chemical characteristics of the sediment matrix are expected (Van Griethuyzen et al., 2003). In particular, changes in oxygenation and redox potential of the superficial sediment layer might result in large changes in the mobility of toxicants, in particular metals (Van den Berg et al., 1998; Charlatchka and Cambier, 2000; Miao et al., 2006). These changes may have a profound effect on the bioavailability of these compounds and therefore on the uptake by and effects on benthic species (Vandecasteele et al., 2005).

The spatial and temporal heterogeneity of pollution is expected to be an important factor influencing settlement and persistence of biota in these newly created benthic habitats (Ivorra et al., 2000; Lu and Wu, 2003; Hunter et al., 2006). However, knowledge on causal relationships between dynamics of toxicant availability in sediments and community effects is superficial: most studies focus on laboratory effects (lacking environmental relevance) or on field monitoring (lacking mechanistic explanations). Therefore, this study sets out to describe the changes in the redox conditions and the mobility of metals in artificially uncovered polluted floodplain sediments under experimental conditions in artificial streams, and to assess the impact of single or recurrent events of toxicant seepage on the colonization, succession and functioning of benthic algae and their communities.

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## 2. Materials and methods

### 2.1. Overview experimental setup

To study the dynamics of metal availability and toxicity of polluted floodplain sediments after flooding under controlled conditions, field collected sediments differing in degree of pollution were transferred to artificial streams. During 10 weeks (in the period April–June 2004), the sediments were flooded with a continuous flow of natural river water and different hydrological conditions (sedimentation and erosion) were simulated. Changes in redox conditions, metal availability and uptake by organisms were quantified and colonization, succession and functioning of the microphytobenthic community was monitored.

### 2.2. Sediment collection

Soil samples were collected from two different sites (located ca 1.5 km from each other) within the Afferdensche and Deestsche Waarden, a floodplain from the river Waal, The Netherlands. Based on available data, differences in degree of metal pollution between these sites were to be expected. Samples were taken in April 2004, when the floodplain was not flooded. At the clean and polluted site, respectively 3 and 6 PVC containers (25 × 25 × 25 cm) were filled with a relatively undisturbed soil core (obtained by removing surrounding soil) from ca. 25–50 cm below the surface (where metals concentrations were highest in the vertical profile (Middelkoop, 2000)) and transported to the artificial streams situated in Lobith. Additional samples were taken for sediment characterization.

### 2.3. Sediment characterization

Grain sizes were quantified using a Laser Particle Sizer (Fritsch A22). C:N ratios were analyzed using a FlashEA 1112 Elemental Analyzer (ThermoQuest) and OM content was measured as loss-on ignition by combustion at 550 °C for 6 h. Total copper and zinc concentrations were determined by means of Flame Atomic Absorption Spectrophotometry (Perkin Elmer 1100B) after digestion in 70% HNO<sub>3</sub> at 100 °C using a DB-#d Driblock (Techne).

### 2.4. Artificial streams

Three artificial streams were constructed to incubate the sediments under controlled flooded conditions. Therefore, the soils samples will from now on be referred to as sediment samples. The streams were designed as a flow-through system, ( $H \times W \times L = 35 \times 27 \times 105$  cm), consisting of a pre-settling basin, a main chamber in which 3 sediment boxes were incubated under a more or less laminar water flow and an outflow basin. They were located outdoors at the RIZA measuring station in the river Rhine (Lobith, The Netherlands) and provided with a continuous flow of natural river water. During the experiments, the sediments were continuously flooded with a layer of ca. 8 cm of water, with a flow rate of approx. 2 cm/s.

### 2.5. Treatments

Four different treatments were included, differing in degree of pollution (clean and polluted) and hydrological regime (simulation of erosion and sedimentation conditions). Each artificial stream contained 3 sediment boxes, 1 filled with clean sediment and 2 filled with sediment from the relatively polluted site. Stream 1 was used to simulate sedimentation conditions. The low current velocity (ca. 2 cm/s) allowed particles (including algae) to settle easily and an algal biofilm could develop without disturbance. The other 2 streams were used to simulate net erosion conditions. The current velocity was similar to stream 1 (ca. 2 cm/s), but every 1 or 2 weeks (see sampling schedule below) the top layer of the sediment was removed by scraping off all material with a putty knife, interrupting succession of the algal biofilm and exposing the bare sediment.

### 2.6. Sampling schedule

In the first 3 weeks of the experiment, sampling was performed every week and after that the sampling frequency was reduced to once per 2 weeks. Sampling included: replacing DGT probes and taking subsamples (sediment cores Ø 3 cm L11 cm) for a) accumulation experiments b) measurements on the colonization, succession and functioning of the algal community and c) toxicity experiments. In addition, in the erosion treatment the top layer of the sediment was removed as described above. The experiment lasted 10 weeks in total.

### 2.7. Redox measurements

To measure redox potential automatically over time at various depths in the sediment without disturbance, we used a (newly

developed) continuous Eh and temperature datalogger (Hypnos). The technical details of this system are described elsewhere (Vorenhout et al., 2004). The datalogger was connected to a probe with eight Eh sensors (placed at -1, 0, 1, 2, 3, 4, 9 and 14 cm depth in the sediment) and 2 temperature sensors (at 0 and 14 cm depth) and a separate calomel reference electrode. Eh values and temperatures were automatically recorded in all treatments every 15 min during the entire 10 weeks of the experiment.

### 2.8. DGT analysis

DGT (diffuse gradients in thinfilms) was used to measure labile species of Cu in situ by immobilizing them in a layer of chelex resin after diffusion through a polyacrylamide gel (Zhang et al., 1998). Providing that the capacity of the resin was not exceeded, the concentration at the resin surface was maintained at effectively zero throughout the deployment, creating a steep concentration gradient in the gel layer. During the deployment time ( $t$ ), concentration of Cu ions in bulk solution ( $C$ ) was calculated using:

$$C = MAq/DtA$$

where  $A$  is the area of the gel membrane,  $M$  is the mass of metal accumulated in the resin layer, determined by means of Flame Atomic Absorption Spectrophotometry (Perkin Elmer 1100B) after digestion of the resin layer in  $\text{HNO}_3$ , and  $D$  is the diffusion coefficient of Cu in this layer (provided by DGTresearch). In this study, commercially available sediment probes (DGTresearch) were used to quantify vertical profiles of Cu-DGT concentrations in the sediment at a vertical spatial resolution of 0.5–1 cm.

### 2.9. Metal accumulation in Tubifex

To each subsample, ca 1 g (wet weight) of Tubifex (obtained from a laboratory culture) was added and incubated at 20 °C. The exposure time was 7 or 14 days, depending on the sampling interval. Tubifex worms were retrieved from the sediment by sieving and allowed to void their guts, total wet weight was determined, and afterwards analyzed for total copper concentrations by means of Flame Atomic Absorption Spectrophotometry (Perkin Elmer 1100B) after digestion of the samples in 70%  $\text{HNO}_3$  and 30%  $\text{H}_2\text{O}_2$  at 100 °C using a DB-#d Driblock (Techne).

### 2.10. Colonization, succession and functioning of the algal community

Algal biomass was quantified by measuring Chl- $a$  content (Lorenzen, 1967) and fluorescence ( $F_0$ ) using a Pulse Amplitude Modulated (PAM) Fluorometer (Waltz). Algal composition was determined by counting algal cells using microscopy. Determination was performed till genus level and genus richness and abundance were subsumed in the Shannon index and differences between treatments were subsequently detected performing individual-based rarefaction using Ecosim v.7.72. (Gotelli and Entsminger, 2006). Functioning of the algal community was quantified by measuring oxygen production (using the light-dark shift method (Glud et al., 1992) with a

rapid oxygen micro-electrode (UniSense OX25). PAM fluorometry was used to determine the maximum photochemical yield of PSII and slope of a PI curve at light intensities ranging from 0–80  $\mu\text{mol photons}\cdot\text{m}^{-2}\cdot\text{s}^{-1}$ , both relative measures of the photosynthetic efficiency (Henley, 1993; Rohacek and Bartak, 1999).

### 2.11. Toxicity test

Growth rates of the diatom *Nitzschia perminuta* in direct contact with the sediment were used as indicator for toxic effects. The samples were first sterilized under UV light, then a fixed inoculum of *N. perminuta* originating from a laboratory culture was added, the overlying water was replaced by algal growth medium, and biomass was measured automatically using the PAM during 4 days. Maximum specific growth rates ( $\mu_{\text{max}}$ ) were calculated as:

$$\mu_{\text{max}} = \ln(F_0t/F_0t_0)/\Delta t$$

where  $F_0$  is an indirect measure for algal biomass at the start of the exponential phase ( $F_0t_0$ ) and at time  $t$  in the exponential phase ( $F_0t$ ) and  $\Delta t$  is the time interval.

## 3. Results

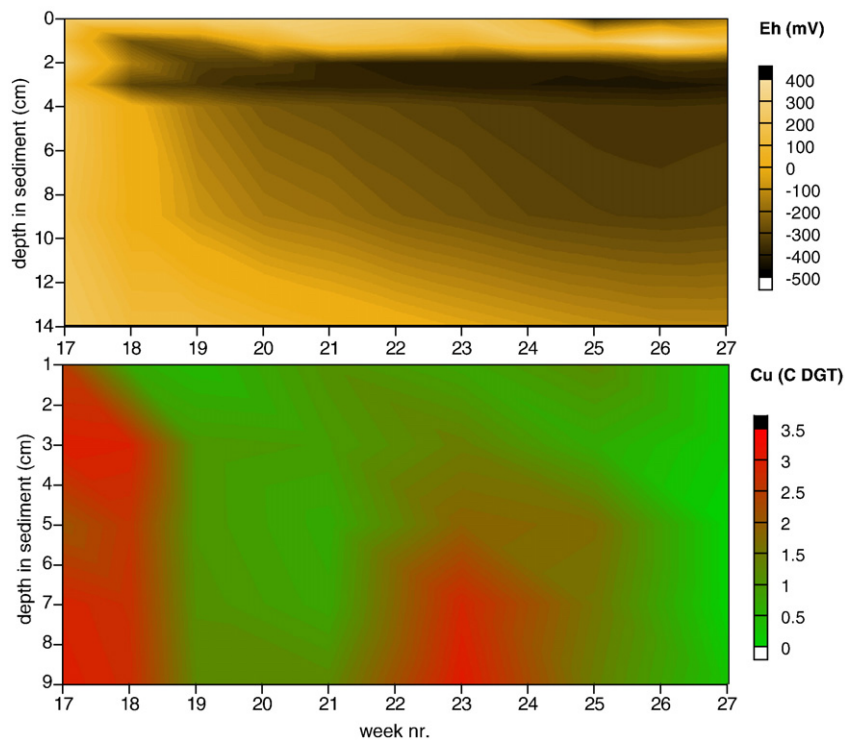
The soil samples collected at the clean reference site and the relatively polluted site were similar in terms of grain size distribution but organic matter content and C:N ratio of the reference site were 2 times lower than at the polluted site. Total Cu and Zn concentrations were more than 10 times higher at the polluted site than at the reference site (Table 1).

Flooding of the floodplain soils caused major changes in the redox potential profiles over time (Fig. 1 top). The top layer at the sediment water interface remained oxidized during the whole period, while the layer just below the surface got reduced very quickly within few days. In deeper layers changes occurred more gradually, even after 10 weeks no steady state profile was reached. With respect to redox conditions, no differences were observed between the different treatments.

The high total concentrations of copper in the polluted sediment are reflected in relatively high available

**Table 1 – Characteristics of the sediments sampled from a relatively polluted site and a clean reference site in the Afferdensche and Deestsche Waarden (a floodplain from the river Waal), The Netherlands**

Coordinates	Reference site		Polluted site	
	N51°53'24" E5°37'59"		N51°53'49" E5°36'45"	
OM (%±SD)	3.5±1.2		8.0±2.0	
C:N	9.6		19.8	
Sand (%)	65		52	
Silt (%)	21		26	
Clay (%)	14		22	
Total Cu (mg/kg)	6		80	
Total Zn (mg/kg)	31		468	



**Fig. 1**–Changes in redox conditions (top graph) and copper concentrations measured by DGT (bottom graph) of floodplain sediment during 10 weeks after flooding in the artificial stream system (flooding started in week 17). The redox contour plot is based on Eh values measured every 15 min at 7 different depths (0–14 cm) and averaged per week and the Cu contour plot is based on DGT concentrations measured every 1 or 2 weeks at 11 different depths (0–9 cm).

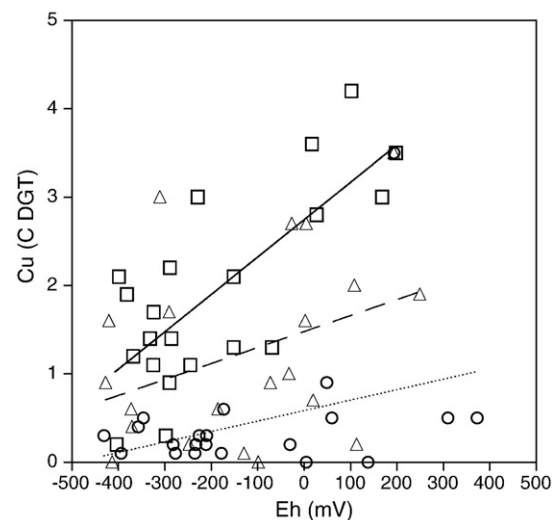
concentrations at the start of the flooding period. However, within 1 week after flooding started, the high concentrations of copper were largely immobilized and no longer available (Fig. 1 bottom). In the reference sediment available copper concentrations were always low.

In the top layer of the sediment, no consistent relationship between redox conditions and available Cu concentrations was found. In the deeper layers of the sediment, however, the availability of copper in the polluted site as measured by DGT showed a relationship with the gradual time and depth related changes in Eh (Fig. 2). This relationship is only significant (linear correlation  $p < 0.05$ ) for the polluted sediment incubated under sedimentation conditions. In the other treatments, available Cu concentrations were on average lower but not significantly related to Eh values.

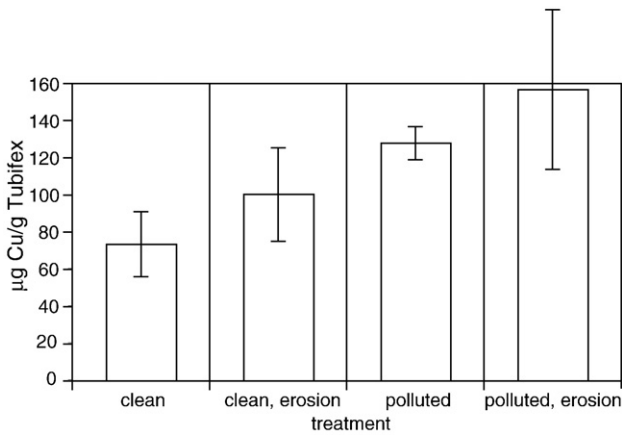
The concentrations of copper in Tubifex worms after 7 days of exposure to the sediments showed significant differences between the clean and polluted site ( $p < 0.05$ ) with higher Cu concentrations in worms in polluted sediments (Fig. 3). Cu concentrations in worms in the erosion treatments were on average higher than from the sedimentation treatments, but these differences were not significant. The concentrations of copper in worms after 7 days of exposure to the sediments were significantly related to copper concentrations in the sediments measured by DGT (linear correlation,  $p < 0.05$ ).

During the 10 weeks of incubation, algal mats developed dynamically in all treatments. Chlorophyll *a* concentrations and PAM fluorescence measurements showed that total algal biomass was determined by accumulation and sloughing

processes resulting in unpredictable differences in biomass over time. Functional characteristics of the biofilm such as the maximum PSII quantum yield, slope of the PI curve and



**Fig. 2**–Changes in Cu-DGT concentrations following changes in the oxidation/reduction in deeper layers (3–9 cm) of a floodplain soil collected from a polluted site (squares, solid line) and a non-polluted reference site (circles, dotted line) after flooding in the artificial stream system. The triangles/dashed line indicate the changes in Cu-DGT in the polluted site incubated under simulated erosional conditions.



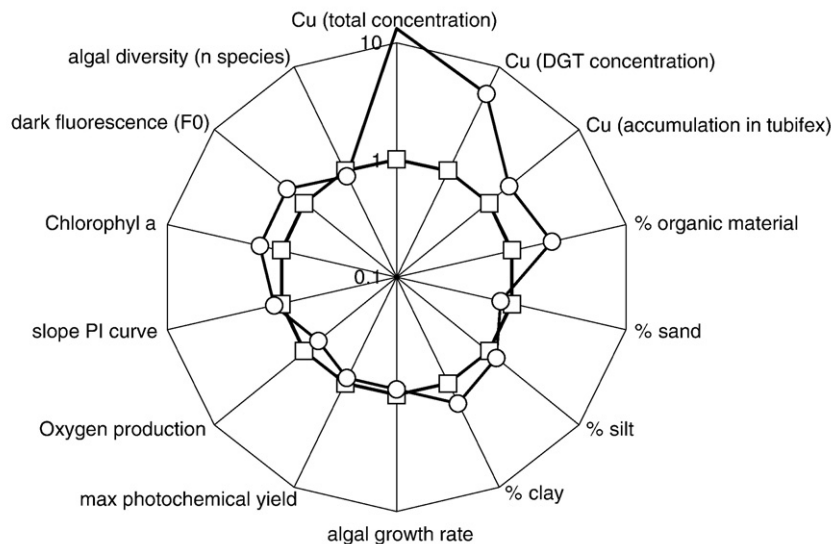
**Fig. 3 – Total concentrations of Cu in *Tubifex* worms exposed during 7 days to samples from a polluted site and a non-polluted reference site incubated in the artificial stream system under normal or simulated erosional conditions. Data represent average values (+/- SD) of 3 repetitive measurements in the first 3 weeks of the experiment.**

oxygen production were more or less constant over time (data not shown). For all investigated parameters, no differences in colonization, succession or functioning became apparent between clean and polluted sediments or between the sedimentation or erosion treatment (Fig. 4). Only eroded sediment, in time, had significantly ( $p < 0.05$ ) reduced biodiversity compared to the non-eroding sediments, but that reduction is not linked to pollution.

#### 4. Discussion and conclusion

The total copper concentration in the sediment collected from the relatively polluted site in the Afferdensche and Deestsche Waarden (80 mg/kg) was below the Dutch environmental intervention value (190 mg/kg) but exceeded the target value (36 mg/kg; 33 mg/kg after correction for clay and organic matter content) and may therefore pose a threat to the environment. Based on extensive research, however, it is widely accepted that risk assessments of sediment associated metals should be based on the bioavailable fraction of these metals (Ankley et al., 1996).

In this study, changes in land use were simulated under controlled conditions to describe spatial and temporal variation in redox conditions and metal bioavailability and relate these changes to uptake and effects. In the deeper layers in the sediment, changes in redox potential towards more reduced conditions after flooding occurred gradually and were found to be predictive for changes in the bioavailability of copper as measured by DGT. Most likely, the decrease in the available fraction of Cu at decreasing Eh values is caused by binding to AVS (Yu et al., 2001) and organic carbon partitioning (Mahony et al., 1996). Conversely, oxidation of organic matter and sulphides may result in copper fluxes out of the sediment with increasing oxygen concentrations (Riedel et al., 1997). In the oxic top layers of sediments, this may result in concentration peaks of dissolved trace metals (Van den Berg et al., 2000). In this study, a strong gradient in redox potential was observed between the top layer of the sediment with oxidized conditions just below the sediment water interface and strongly reduced conditions directly underneath. However, after only



**Fig. 4 – Floodplain sediments collected from a polluted site (circles) compared relatively to floodplain sediments collected from a clean reference site (squares; set to 1). Overview of the different parameters (averages of all observations) representing the physical characteristics of the sediment (% OM, particle size distribution), the degree of pollution (total and DGT-Cu concentrations, accumulation in *Tubifex*), the effect of single algal species (growth rate) and the effects on structural (species diversity) and functional characteristics (F0, Chlorophyll a concentration, slope PI curve, oxygen production and maximum photochemical yield) of the algal biofilm that developed on these sediments in the artificial stream experiment.**

1 week of flooding, DGT concentrations of copper in the top layers were always low and no relationship between redox potential and bioavailability of copper was found. Remobilized copper might be scavenged by Mn- and Fe-(hydr)oxides near the sediment water interface (Van den Berg et al., 2000) or aqueous concentrations of copper can be washed out of the sediment by the continuous flow of water. Similar observations were made by Ahumada and Schalscha (1993) who determined the chemical fractionation of metals and found no increase in available forms of added Cu at increasing Eh values. Moreover, Miao et al. (2006) reported decreasing aqueous Cu concentrations in sediments following oxidation of sediment. Generally, many factors may influence the relationship between Eh and metal bioavailability, such as changes in pH and buffering capacity of the sediment (Chuan et al., 1996; Charlatchka and Cambier, 2000; Chen and Lin, 2001) or concentrations of redox sensitive compounds, microbial activities and early diagenetic processes (Van den Berg et al., 2000). In addition, this study demonstrated that within a vertical profile of one specific sediment type, there is also no simple relationship between the bioavailability of copper and redox conditions.

DGT was used to measure the labile fraction of copper. Previously it was demonstrated that DGT derived copper concentrations in soil are in good agreement (but lower) than copper concentrations measured in soil solution directly (Zhang et al., 1998) and a good predictor for copper availability to plants (Zhang et al., 2001). In this study, a significant correlation was found between copper DGT measurements and copper concentrations measured in benthic organisms (*Tubifex*), but only for data collected in the first 3 weeks of the experiment when rapid changes in the bioavailability of copper were observed. Due to high initial internal copper concentrations in the *Tubifex* worms (being equal or slightly higher than internal concentrations in worms after exposure to the reference sediments) and differences in exposure times, variation in metal uptake over the entire experimental period could not be solely contributed to changes in available copper concentrations in the sediments.

The differences in total metal concentrations between sediments from the reference site and from the polluted site were not reflected in any of the measured biological parameters (Fig. 4). Several parameters were selected to search for potential effects of the sediment associated metals on the colonization, succession and functioning of benthic algae and their communities. The OECD growth inhibition test with microalgae (OECD guideline 201) is one of the most common ways to test for potential toxic effects of chemicals. Here, this test was modified (using benthic diatoms in direct contact with the sediments) but no delayed or reduced growth rate could indicate a reduced colonization potential of microalgae on the polluted sediment. This corroborates with the observations on algal biofilm development during the course of the experiment. Differences in biodiversity, succession and total biomass were found, but these differences were not related to total or available copper concentrations. Also the functioning of the algal biofilm in terms of photosynthetic efficiency or primary production was not impaired on the polluted sediments, although copper blocks electron transport in PSII and is considered to be a very effective algicide (Murray-

Gulde et al., 2002). If the total amount of copper present in the sediment was available as free ions in the sediment pore water, concentrations would be more than 3 orders of magnitude higher than reported effect concentrations (Barranguet et al., 2000). Based on the Cu-DGT measurements, however, it was demonstrated that available concentrations of metals in interstitial waters were low and hence biological impacts were undetectable. Similarly, due to low bioavailability, recolonization by benthic organisms was not affected on field incubated metal spiked freshwater (Boothman et al., 2001) and marine (Hansen et al., 1996) sediments.

In conclusion, the availability of copper in floodplain sediments shows a very high variability in relation to uncovering and flooding of polluted sediments. Polluted sediments showed more than ten-fold higher levels of total copper, yet this difference shows up only partially when comparing the available copper fraction as measured by DGT, while introduced *Tubifex* showed only marginally different levels of accumulated copper. Colonization, growth and succession of algal communities on polluted sediments was not impaired. These observations illustrate that risk assessment of polluted sediments in dynamic environments should be based on available fraction of metals. Changing environmental conditions, such as flooding, can result in stable chemical conditions with low a bioavailability of metals and hence in a diminution of actual ecological risks.

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