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# Trace metal behaviour in estuarine and riverine floodplain soils and sediments: A review

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## ABSTRACT

This paper reviews the factors affecting trace metal behaviour in estuarine and riverine floodplain soils and sediments. Spatial occurrence of processes affecting metal mobility and availability in floodplains are largely determined by the topography. At the oxic–anoxic interface and in the anoxic layers of floodplain soils, especially redox-sensitive processes occur, which mainly result in the inclusion of metals in precipitates or the dissolution of metal-containing precipitates. Kinetics of these processes are of great importance for these soils as the location of the oxic–anoxic interface is subject to change due to fluctuating water table levels. Other important processes and factors affecting metal mobility in floodplain soils are adsorption/desorption processes, salinity, the presence of organic matter, sulphur and carbonates, pH and plant growth. Many authors report highly significant correlations between cation exchange capacity, clay or organic matter contents and metal contents in floodplain soils. Iron and manganese (hydr)oxides were found to be the main carriers for Cd, Zn and Ni under oxic conditions, whereas the organic fraction was most important for Cu. The mobility and availability of metals in a floodplain soil can be significantly reduced by the formation of metal sulphide precipitates under anoxic conditions. Ascending salinity in the flood water promotes metal desorption from the floodplain soil in the absence of sulphides, hence increases total metal concentrations in the water column. The net effect of the presence of organic matter can either be a decrease or an increase in metal mobility, whereas the presence of carbonates in calcareous floodplain soils or sediments constitutes an effective buffer against a pH decrease. Moreover, carbonates may also directly precipitate metals. Plants can affect the metal mobility in floodplain soils by oxidising their rhizosphere, taking up metals, excreting exudates and stimulating the activity of microbial symbionts in the rhizosphere.

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## 1. Introduction

Riverine and estuarine floodplains are formed by the periodical deposition of suspended sediments from river water during flood events. Although soils of many floodplains

already started to develop before human settlement, major sedimentations were initiated after human settlement, and subsequent deforestation and cultivation of land, causing significantly increased erosion rates in the catchment area. Particular areas, especially in tidal estuaries, have been

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frequently flooded for a long time, which resulted in a long lasting sedimentation of suspended particles. These areas are called tidal flats if they are submerged during every high tide. Because of continued sedimentation, these tidal flats get banked up higher over time. At some point, they are only submerged during spring tides and vegetation starts to develop. Such marshes are crossed with gullies that allow the water to penetrate deep into them during every tidal cycle. As a result of such intense interactions between the soil and its aquatic environment, floodplain soils can be considered as semi-terrestrial soils with aquatic or epiaquatic moisture regimes. They are considered to be shaped by various aquatic sources including groundwater, static water, return seepage and flood water, and frequently host unique ecosystems.

Large variation in flood water characteristics and flooding frequency (from up to twice a day or nearly continuously submerged to once in several years) of floodplains is observed. This results in large variation in sedimentation rates for particular areas. Floodplains as natural ecosystems are not separated from the river by dikes, but human activity may have changed these systems by river embankment or impoldering of tidal marshes. These changes resulted in lower flooding frequency and sedimentation rates. Sometimes, flooding frequency is determined by man, e.g., for alluvial plains along embanked rivers only flooded at extremely high water levels, or planned winter floodings as a historical agricultural practice in the past.

Because of their generally high fertility, some floodplain soils have also been intensively used for agriculture and silviculture for a long time. However, since scope, duration and frequency of floods are hardly predictable, almost any commercial use of floodplains, including agriculture, is very risky. Therefore rivers have been embanked to reduce the flooding frequency of the alluvial plains used for agriculture or tidal marshes were impoldered for the same reason. Today, an additional considerable risk is associated with the often very high levels of trace metals in floodplain soils (e.g., [Rinklebe et al., 1999, 2002](#); [Friese et al., 2000](#); [Böhme et al., 2005](#); [Devai et al., 2005](#); [Du Laing et al., 2007a](#); [Overesch et al., 2007](#); [Rinklebe et al., 2007](#)). These metals were carried along with the river water and sediments, and originate from various sources in the catchment area such as industrial or mining activities, agricultural non-point sources, or natural, geogenic processes (e.g., [Kowalik et al., 2003](#); [Förstner et al., 2004](#)). Also atmospheric deposition can contribute to contamination of floodplains with trace elements.

The presence of metals requires appropriate risk assessment of tidal wetland ecosystems and floodplains used for agriculture ([Vandecasteele et al., 2006](#)). Most current environmental standards and sanitation thresholds for soils and sediments are still based on measuring total metal concentrations. Total levels alone do not allow assessing short term environmental risks because they do not reflect the mobility, reactivity, or bioavailability of potentially toxic trace elements ([Rieuwerts et al., 1998](#); [Sauvé et al., 2000](#)). The behaviour of trace elements is to a large extent determined by their chemical forms of occurrence. General chemical forms of elements in soils and sediments include ([Gambrell, 1994](#)):

- water-soluble metals, as free ions, inorganic or organic complexes;

- exchangeable metals;
- metals precipitated as inorganic compounds, including insoluble sulphides;
- metals complexed with large molecular-weight humic materials;
- metals adsorbed or occluded to precipitated hydrous oxides;
- metals bound within the crystalline lattice structure of primary minerals.

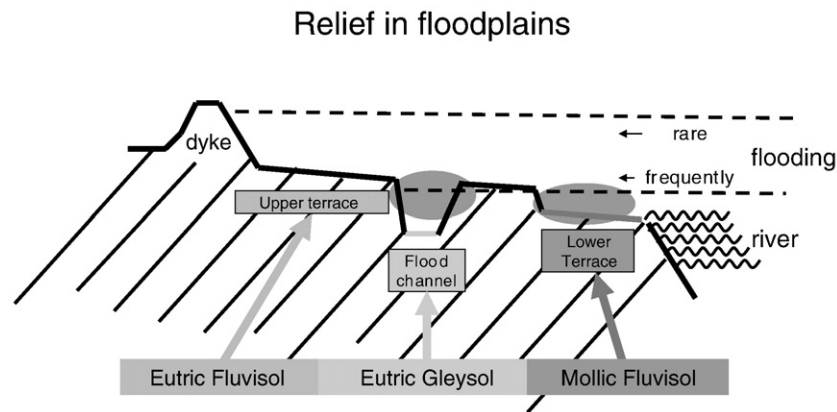
As a result, metal fate in soils and sediments is governed by numerous processes, including sorption/desorption, precipitation/dissolution and complexation/decomplexation.

Three zones may be distinguished in sediments and floodplain soils: an oxic layer, an anoxic layer and an oxic–anoxic interface ([Salomons et al., 1987](#)). In the oxic surface water and sediment or floodplain soil layers, stable phases of trace metals are mostly sorbed species. Important sorbing phases are Fe/Mn hydroxides, carbonates, organic matter and clay minerals. Salinity and the presence of soluble organic components in the pore water are prime factors affecting desorption from these phases. The oxic–anoxic interface and the anoxic layer beneath the oxic layer play major roles in the potential flux of trace metals from sediments or floodplain soils to surface waters. In these layers, especially redox-sensitive processes occur, which mainly result in the inclusion of metals in precipitates or the dissolution of metal-containing precipitates. Kinetics of these processes are of great importance for tidal floodplain soils as the location of the oxic–anoxic interface is subject to change due to fluctuating water table levels ([Du Laing et al., 2007b](#); [Rinklebe et al., 2005](#)). The local variability of water table levels depends on the flood frequency and duration, which is closely related to the topography of the floodplain area. The latter also primarily affects the variability of metal accumulation within the floodplain area.

## 2. Floodplain topography affecting trace metal pollution levels

In floodplains, metal accumulation and the spatial occurrence of processes affecting metal mobility and availability are largely determined by the topography. Topography is indeed a key soil-forming factor (e.g., [Bockheim, 2005](#); [Bockheim et al., 2005](#); [Lin et al., 2006](#)). Differences in the topography of floodplains often result in important hydrological and pedological differences (Fig. 1).

Dominating soils in many floodplains are Eutric Fluvisols (FAO/ISRIC/ISSS, 1998) (Fig. 1). These can be considered as fluvial loamy terraces. In turn, Eutric Gleysols (FAO/ISRIC/ISSS, 1998) are characteristic soils in the flood channels, depressions, and ditches which are embedded in these fluvial loamy terraces. They are often submerged for a longer time and can show gleyic, fluvic and stagnic properties ([Rinklebe, 2004](#)). Eutric Gleysols consist of floodplain silt and clay, and frequently reveal high organic carbon contents. Due to the association of metals with clay and organic matter (e.g., [Du Laing et al., 2007a](#)), their accumulation is often higher in the soils of the flood channels, depressions, ditches, and furrows than in the soils of the upper terraces (Eutric Fluvisols),



**Fig. 1**–Characteristic topographical scheme of relief in floodplain ecosystems, their water regime and the linked type of soils, classification according to [FAO/ISRIC/ISSS \(1998\)](#).

although heterogeneity within soil types is often high and smooth transitions between them exist ([Rinklebe, 2004](#); [Walder et al., 2008](#)). Periodic flooding, concurrent erosion and sedimentation control the accumulation and dynamics of substances, including the content and chemistry of pollutants. A long duration of flooding with decelerated flow-rates, including stagnant water, results in sedimentation of mainly fine-grain sediments as well as considerable amounts of organic matter ([Rinklebe, 2004](#)).

Mollic Fluvisols ([FAO/ISRIC/ISSS \(1998\)](#)) are common on the lower-laying terraces ([Rinklebe, 2004](#); [Rinklebe et al., 2007](#)) ([Fig. 1](#)). They consist of floodplain silt and reveal high contents of soil organic carbon and a high microbiological activity ([Rinklebe and Langer, 2006, 2008](#)) down to a depth of 1 m or more. Moreover, they do not become massive or hard when they are dry ([FAO/ISRIC/ISSS, 1998](#); [Rinklebe, 2004](#)). The elevated humus content is the result of the additive effect of fluvial-transported material with a high organic matter content (sedimentary organic matter) on the one hand, and with an increased on-site formation of humus resulting from a high phytomass production on the other. In floodplain soils, the accumulation of carbon is generally higher than that of terrestrial soils ([Rinklebe, 2004](#); [Rinklebe et al., 2007](#)), which should be taken into consideration in model calculations on carbon sequestration ([Eisenmann et al., 2003](#)). Increased biomass production rather than a reduced decomposition often seems to cause increasing soil carbon contents. Mollic Fluvisols are characterised by a high bioturbation and a stable aggregate fabric ([Rinklebe, 2004](#)). Concentrations of many pollutants are considerably higher in Mollic Fluvisols than in Eutric Fluvisols ([Rinklebe et al., 2007](#)). In general, concentrations of pollutants often reveal the following sequence:

Mollic Fluvisol  $\geq$  Eutric Gleysol  $\geq$  Eutric Fluvisol

With sufficiently detailed soil maps, general patterns of pollutant concentrations in floodplain ecosystems can thus be predicted. The quality of prognosis depends on the spatial scale ([Dobermann et al., 1997](#); [Franke and Rinklebe, 2003](#); [Schindler et al., 2007](#)). Moreover, topography, water regime, geology, soil and substrate type, land use, climate, vegetation, and site-specific peculiarities must be considered when

evaluating the prediction accuracy, as well as the importance of various processes affecting metal mobility and availability at a particular site. Moreover, human changes on floodplain topography (e.g., embanked rivers and impoldered tidal marshes) may affect sedimentation and thus pollution levels.

### 3. Factors affecting trace metal mobility and availability in floodplain soils

#### 3.1. Adsorption and desorption

Electropositively charged elements can be attracted to negatively charged surfaces of organic matter, clay particles and Fe and Al oxides, which determine the cation exchange capacity (CEC) ([Evans, 1989](#)). A high CEC therefore reduces metal mobility and availability and increases metal cation retention. Consequently, many authors report highly significant correlations between CEC, clay or organic matter contents and metal contents of floodplains soils or sediments ([Horowitz et al., 1989](#); [Callaway et al., 1998](#); [Shriadah, 1999](#); [Du Laing et al., 2007a](#)). A study of a number of river systems showed that Fe/Mn hydroxides were the main carriers for Cd, Zn and Ni under oxic conditions, whereas the organic fraction was most important for Cu ([Salomons et al., 1987](#)). In the simplest form, the sorption mechanism assumes a single stage in which dissolved metals in the bulk solution attain rapid equilibrium with weak binding sites on the surfaces of particles. However, supplementary, slower stages can also be hypothesized in which the metals migrate into the pores and/or undergo solid-state reactions to higher-energy binding sites ([Fig. 2](#)). The time constants of the latter reactions are however relatively long and may cover the range of estuarine flushing times. This suggests that if the supplementary stages are accounted for, it is unlikely that a dissolved constituent will be in true equilibrium with the particulate phase during typical estuarine flushing times ([Millward and Liu, 2003](#)).

#### 3.2. Effect of salinity

Tidal variations in estuaries can result in important location-specific variations in salinity of river water and pore water of



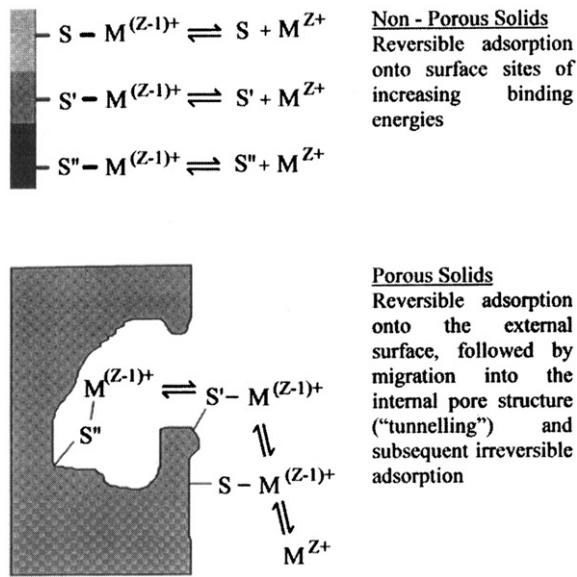


Fig. 2 – Sorption mechanisms for uptake of dissolved metals by non-porous and porous solids. S, S' and S'' are binding sites of increasing energy and  $M^{Z+}$  is a dissolved metal (reproduced from Millward & Liu, 2003, with permission from Elsevier).

floodplain soils and sediments. Trace metals can be mobilised as soluble chloride complexes (Hahne and Kroontje, 1973). The stability and solubility of in particular  $CdCl_2$  complexes is relatively high while the affinity for sorption to the solid soil phase is low (Doner, 1978; Comans and Van Dijk, 1988). Upon the formation of these complexes, the activity of free  $Cd^{2+}$  in the solution will decrease and desorption will increase. Only Cd that is rather weakly bound to the solid soil phase will be desorbed as

a result of chloro-complexation (Paalman et al., 1994). Besides the effects of complexation, an increase of the salinity is associated with an increase in the concentrations of major cations (Na, K, Ca, Mg) that compete with heavy metals for the sorption sites (Tam and Wong, 1999). According to Khattak et al. (1989), the addition of Ca-salts results in a higher release of exchangeable metals in the soil solution compared to the addition of Na-salts, which are less competitive for sorption. Balls et al. (1994) observed increasing Cd desorption from the particulate phase with increasing salinities in the Forth estuary (Scotland), whereas Geringa et al. (2001) found that high salinities resulted in a faster release of Cd from CdS during the oxidation of reduced sediments of the Scheldt estuary (Belgium and The Netherlands). This release was found to be stimulated by both formation of chloride complexes and ion exchange. Du Laing et al. (2008b) reported that such effects of salinity on the Cd mobility and availability only occur in oxidised, i.e. sulphide-poor, sediments. Gambrell et al. (1991b) also studied salinity effects during the oxidation of reduced metal-polluted brackish marsh sediments. Soluble Cd, Cr and Cu were found to enhance with increasing salinity, whereas the salinity did not significantly affect Ni and Pb mobility. According to Millward and Liu (2003), the extent of metal desorption from sediments which were suspended in seawater followed the general order  $Ni > Cd > Zn > Cu$ , whereas Lores and Pennock (1998) concluded that salinity affected the binding of metals to humic acids in the Suwannee River. Binding of Cd, Cr, and Zn to humic acids decreased to less than 20% at salinities increasing up to 15 psu. Copper binding however decreased to 27% at a salinity of 3 psu, whereas it increased again to 60% at a salinity of 15 psu. This would be due to complex interactions between salinity, humic acids, pH and Cu, which have also been noted by Geringa et al. (1998) in the saline part of the Scheldt estuary (Belgium and The Netherlands).

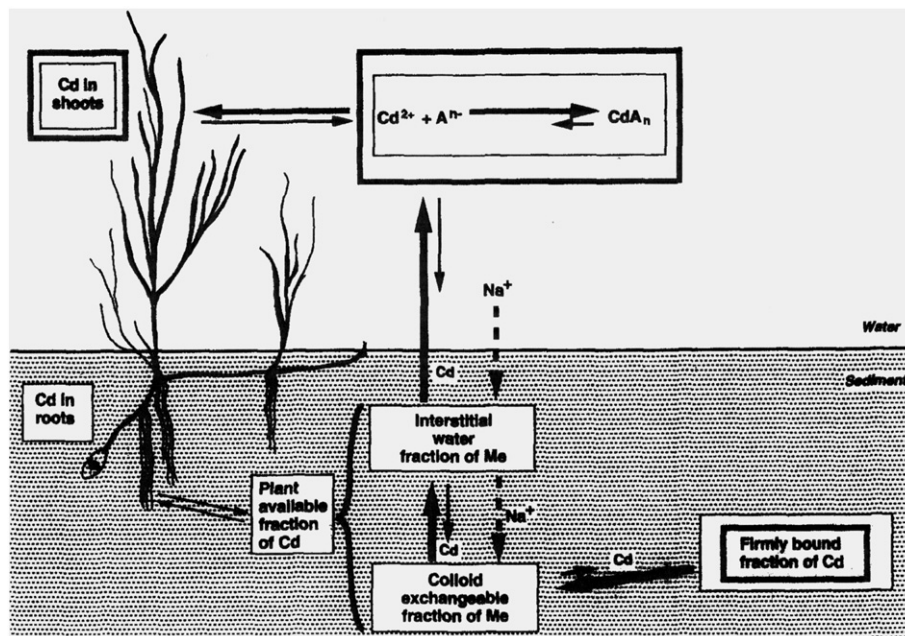


Fig. 3 – Conceptual model of Cd translocation in a macrophyte–water–sediment system at increasing salinity of the water. Change in concentration of Cd denoted with bold squares and changes in equilibrium denoted with bold arrows (adapted from Greger et al., 1995, with permission from Elsevier).

The salinity affects dissolved metal speciation and toxicity in surface waters. [Verslycke et al. \(2003\)](#) reported a decreasing toxicity to the estuarine mysid *Neomysis integer* upon increasing the salinity from 5 to 25‰ and attributed this to lower activities of the free trace metal ions. The effect was strongest for Cd and Pb and was attributed to their complexation with chloride ions. The toxicity of Ni, Cu, and Zn was affected to a smaller extent by salinity. [Greger et al. \(1995\)](#) studied the effect of salinity on the uptake of Cd by the submerged macrophyte *Potamogeton pectinatus* from both water and sediments. They constructed a conceptual model for Cd uptake by an aquatic plant, which is represented in [Fig. 3](#). Cadmium uptake from water was found to decrease when increasing salinity up to 10‰. However, in the presence of sediments, Cd uptake increased with rising salinity. This clearly illustrates that ascending salinity promotes Cd desorption from sediments, hence increases total Cd concentrations in the water column and Cd uptake by organisms. This corresponds also with findings of [Du Laing et al. \(2002\)](#), who found increasing Cd concentrations in ground-dwelling spiders living on estuarine marshes with increasing salinities. Once in the water column, further increasing salinities however promote the formation of Cd chloride complexes, which seem to be less bio-available compared to free Cd<sup>2+</sup>. As a result, a higher Cd bioavailability and toxicity with decreasing salinity was previously observed for organisms living in close contact with the water column, such as mussels ([Fischer, 1986](#); [Stronkhorst, 1993](#)) and invertebrates ([McLusky et al., 1986](#)). [Zanders and Rojas \(1996\)](#) concluded that the accumulation of Cd in the tissues of fiddler crabs is also enhanced under conditions of low salinity surface water. They did not only attribute this effect to increased concentrations of Cd<sup>2+</sup> forms, but also cited the decreased competition of Ca<sup>2+</sup> for transport sites (e.g., [Wright and Frain, 1981](#)), permeability changes of the animal's surfaces in response to environmental salinity levels (e.g., [Chan et al., 1992](#)), and the source of the metal (either dietary or in solution, e.g., [Pratap and Wendelaar-Bonga, 1993](#)) as factors affecting Cd uptake by organisms under changing salinities.

### 3.3. Adsorption, complexation and chelation to organic matter

Decaying plant material causes litter to accumulate on floodplain soils ([Fig. 4](#)). This litter will contribute to the binding of metals by adsorption, complexation and chelation ([Alvim Ferraz and Lourenço, 2000](#); [Du Laing et al., 2006](#)). At the same time, dissolved organic ligands, such as low to medium molecular weight carboxylic acids, amino acids and fulvic acids, can form soluble metal complexes. The net effect of the presence of organic matter can either be a decrease or an increase in metal mobility.

An enhanced mobilisation of metals as dissolved organic complexes was observed for Ni ([Tipping et al., 1998](#); [Wells et al., 1998](#)), for Pb, Cu and Zn ([Alvim Ferraz and Lourenço, 2000](#)), and for Hg, Cr, Cu and As, but not for Cd and Zn ([Kalbitz and Wennrich, 1998](#)). [Charlatchka and Cambier \(2000\)](#) found that Pb was especially complexed by organic acids in a flooded soil. Reversely, high molecular weight organic matter compounds in the solid soil phase can reduce the metal availability ([Gambrell, 1994](#)). Moreover, microorganisms in the rhizosphere of wetland plants can accumulate metals ([Scholes et al., 1999](#)). [Decho \(2000\)](#)

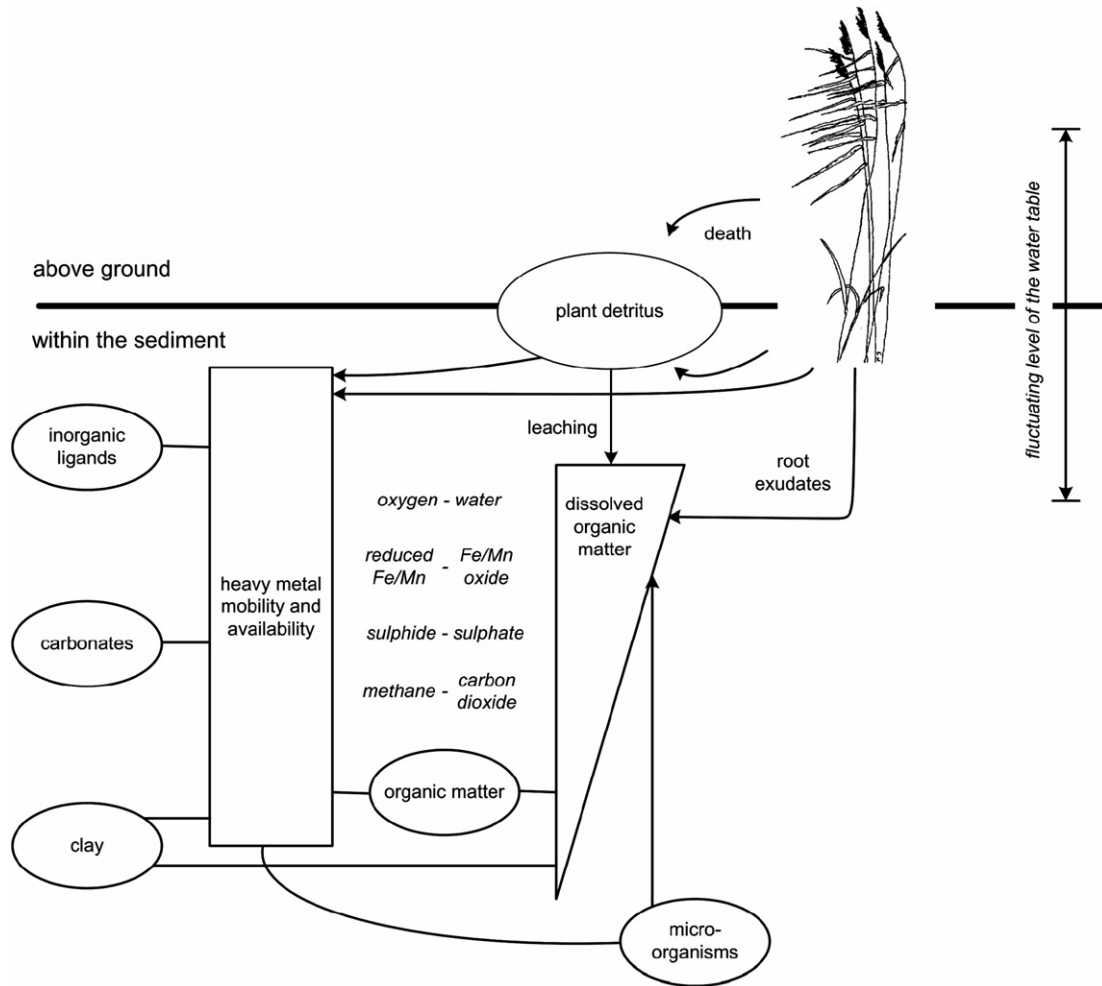
reported a significant role of extracellular microbial polymeric secretions (microbial biofilms) in intertidal systems, both in the binding and concentration of metal contaminants, as in the trophic transfer of metals to the food web. According to [Kunito et al. \(2001\)](#), these exopolymers were especially produced in large quantities by Cu-resistant bacteria in the rhizosphere of wetland plants, which suggest its involvement in the detoxification of Cu. Finally, organic matter indirectly affects metal fate by forming a food source for microorganisms which catalyse a series of redox reactions in the presence of electron acceptors. These reactions primarily affect the mobility and availability of metals in the wetland soils ([Fig. 4](#)).

### 3.4. Precipitation/dissolution of metals upon changing redox conditions

#### 3.4.1. Redox processes occurring during flooding

Particularly in wetland ecosystems, oxidation and reduction reactions are of prime importance. Water saturation during extended periods of time usually results in changes in chemical properties of sediments and soils, as well as in microbial populations and processes. Soils tend to undergo a series of sequential redox reactions when the redox status of the soil changes from aerobic to anaerobic conditions during flooding. Major reactions include denitrification, manganic manganese [Mn (IV)] reduction, ferric iron [Fe (III)] reduction, sulfate (SO<sub>4</sub><sup>2-</sup>) reduction, and methanogenesis ([Fig. 4](#)). These processes are catalysed by microorganisms ([Paul and Clark, 1996](#)) and have previously been extensively studied and reviewed (e.g., [Patrick and DeLaune, 1972](#); [Ponnamperuma, 1972](#); [Smith and DeLaune, 1984](#); [Reddy et al., 1989](#); [Patrick and Jugsujinda, 1992](#)). The intensity of soil reduction can be rapidly characterized by the oxidation–reduction potential (redoxpotential, E<sub>H</sub>), which is a measure for the electron availability and allows the prediction of the stability and availability of various metals in floodplain soils and sediments. It evolves from high to low when the redox status of the soil changes from aerobic to anaerobic conditions during flooding.

Metals respond in different ways to changes in E<sub>H</sub>. Marsh sediments tend to rapidly reduce the very toxic Cr(VI) to less toxic trivalent Cr ([Pardue & Patrick, 1995](#)). Moreover, [Simpson et al. \(2000\)](#) observed the reduction of Cu(II) to Cu(I) under slightly alkaline conditions and negative redox potentials, whenever a suitable electron donor species is present. In natural sediments, numerous electron donors (e.g., Fe(II), sulphur compounds), and bacteria acting as catalysts, may be actively involved in the Cu(II) to Cu(I) reduction process, subsequently leading to Cu<sub>2</sub>S precipitation. However, changes of the valence state as a result of E<sub>H</sub> changes in natural sediments are not observed for most of the metals, including Cd and Zn, which are important from an eco-toxicological point of view. Their mobility can also be significantly affected by E<sub>H</sub> changes. This can be a result of, e.g., redox-induced changes to the metal-binding capacity of humic materials, insoluble metal sulphide formation (or sulphide oxidation) and changes in Fe/Mn-oxyhydroxides, which are known to be effective in immobilizing some metals under oxidizing conditions ([Du Laing et al., 2008a](#)). Cadmium, e.g., is reported to be much more mobile and plant-available in oxidized soils and sediments compared to reduced conditions ([Gambrell et al., 1991a,b](#); [Vandecasteele et al., 2007a](#)).



**Fig. 4– Overview of possible interactions and factors affecting metal mobility and availability in soils of wetlands, dominated by the presence of vegetation (reproduced from Du Laing, 2006, with permission from the author).**

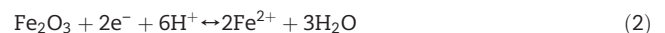
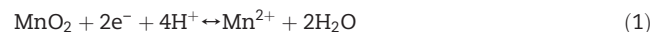
A change in redox conditions may also affect the soil pH. During reduction, protons are being consumed, whereas during oxidation acidification tends to occur. In turn, these pH changes might affect metal mobility and availability. A pH drop prevents the transfer of most trace metals to the sediment and/or causes a desorption from the sediments (e.g., Salomons et al., 1987; Gambrell et al., 1991b; Calmano et al., 1993). A higher activity of protons reduces the negative surface charge of organic matter, clay particles and Fe and Al oxides and increases the solubility of precipitates, such as sulphides.

In floodplain soils, kinetics of the above-mentioned processes are of great importance as the location of the oxic-anoxic interface is subject to change due to fluctuating water table levels. Therefore, studies on factors affecting metal fate in floodplain soils should focus on these kinetics by including sampling programs with a sufficiently high spatial and temporal resolution.

#### 3.4.2. Metal fate as affected by oxidation and reduction of Fe and Mn

In an oxic environment, Fe and Mn will precipitate as Fe or Mn oxides. Trace metals can co-precipitate or adsorb to these oxides. Nickel was, e.g., reported to primarily co-precipitate

with Mn oxides by Zwolsman et al. (1993) in salt marsh sediments from the Western Scheldt, whereas Guo et al. (1997) reported an increasing affinity between Fe and Mn oxides and As, Cd, Cr and Zn with increasing sediment redox potential. Reduction and solubilisation of these oxides, as presented in Eqs. (1) and (2), can in turn have important consequences for the mobility of metals.



This has been reported for Pb, Zn and Cd by Davis and Kent (1990) and for Ni by Kashem and Singh (2001) and Du Laing et al. (2007b). The association of Cr, Cd and Zn with insoluble large molecular humic substances subsequently increased, as well as the association of Cd and Zn with carbonates and sulphides. The stability of  $\text{Fe}^{2+}$  and Fe (hydr)oxides primarily depends on a combination of  $E_H$  and pH of the sediment. The nearly amorphous  $\text{Fe}(\text{OH})_3$  minerals (ferrihydrite) are reduced at a higher  $E_H$  for a given pH than do the crystalline minerals of  $\text{FeOOH}$  (goethite) or  $\text{Fe}_2\text{O}_3$  (hematite). Generally, Fe occurs in soluble forms in an acid environment. When a neutral pH is approached, Fe only can exist in solution at low redox potentials,



or as a soluble organic complex in oxic soils. Some bacteria can catalyze these reductions (Lovley and Phillips, 1988b). Some authors, such as Lovley and Phillips (1988a), reported that the reduction of Fe<sup>3+</sup> does not begin before all Mn<sup>4+</sup> is depleted. However, Patrick and Jugsujinda (1992), Peters and Conrad (1996) and Du Laing et al. (2007b) observed at least some overlap.

#### 3.4.3. Metal fate as affected by sulphur cycling

The mobility and availability of metals in a floodplain soil can be significantly reduced by the formation of metal sulphide precipitates, which can occur if the sedimentary medium becomes (super)saturated with respect to sulphides. These sulphides are produced by reduction of sulphates (Eq. (3)) upon the creation of anaerobic conditions. The sulphates mainly originate from the flooding water, especially in estuaries (Du Laing et al., 2007b), or they can be locally released during organic matter decomposition (Neue and Mamaril, 1985). Du Laing et al. (2008a) reported that the depth at which sulphide precipitation significantly contributed to metal accumulation in sediments of intertidal reed beds along the Scheldt estuary depended on the sampling location and sediment characteristics, and varied from less than 5 cm below the surface in clayey, organic sediments to more than 1 m in sandy sediments.

Sulphate reduction is initiated by microbial communities at quite low redox potentials, below –150 mV (Gambrell et al., 1991a; Mansfeldt, 2004) or –220 mV according to Ross (1989). It leads to the formation of elemental sulphur and sulphides.



Iron is usually the most predominant element which generates sulphide precipitates. It is released from reducible minerals such as oxides/oxihydroxides within the sedimentary layers, in which sulphate reduction occurs, to give ferrous Fe. This subsequently reacts with the dissolved H<sub>2</sub>S to produce amorphous FeS and/or crystallized FeS (such as mackinawite and greigite), which are considered as precursors for pyrite formation (FeS<sub>2</sub>) (Billon et al., 2001).

Experimental studies in subtidal marine sediments (Wes-trich and Berner, 1984) have shown that in the presence of high levels (>5 mM) of sulphate, typical in the marine environment, organic carbon availability most often limits further microbiologically mediated sulphate reduction. As a result, marine sediments are often depleted in degradable organic matter. There is still sulphate in their pore waters, whereas all reducible Fe is converted to Fe sulphide. The methanogenic state is reached only at very great depths (Salomons et al., 1987). Sulphates may be limiting at higher depths in some highly organic marine and brackish sediments, where sulphate is exhausted by sulphate-reducing bacteria, or in freshwater environments, where sulphate concentrations are lower. Moreover, the formation of pyrite is not favoured in freshwater systems (van den Berg and Loch, 2000). A model of Lovley and Klug (1986) predicts that sulphate reduction in freshwater lake sediments becomes limited when sulphate concentrations in the pore water drop below 30 μmol L<sup>-1</sup>. In these conditions, methanogenic bacteria out-compete sulphate reducers for common substrates (White et al., 1989). Additionally, sulphate reduction is slowed down in the presence of Fe reducing microorganisms (Lovley and Phillips,

1987). As a consequence, Fe hydroxides are only to a limited extent converted to sulphides, whereas the methanogenic state is reached relatively fast and the available reduced Fe is precipitated as siderite (FeCO<sub>3</sub>) (Salomons et al., 1987).

The degradation of organic matter and the transformation of Fe hydroxides to Fe sulphides and siderite (FeCO<sub>3</sub>) in the anoxic layer cause a reduction in the total adsorption capacity of the solid sediment phase for trace metals. However, the production of hydrogen sulphide and the high alkalinity allows for the precipitation of stable metal sulphides, or carbonates in the absence of sulphate. The possible formation of trace metal sulphides and reaction of trace metals with Fe sulphide minerals has been thoroughly documented. During the sulphidation process some trace metals, that are liberated from sedimentary components such as organic matter and metal oxides, can adsorb onto or co-precipitate with FeS minerals or can precipitate directly as discrete solid phases (Billon et al., 2001). Copper, Zn and Cd are especially expected to occur as CuS, ZnS and CdS in marine and estuarine anoxic sediments, because sulphate is highly available in these environments. This was concluded from, e.g., adsorption experiments with and without sulphide present. Zinc, Cu, Ni and above all Cd were found to be only weakly pyritized, whereas Mn is well pyritized (Huerta-Diaz et al., 1998; Billon et al., 2001). Guo et al. (1997) observed increasing association of Cd and Zn with sulphides, next to carbonates and insoluble large molecular humic substances with decreasing redox potentials, whereas Cr association was restricted to insoluble large molecular humic substances. Zwolsman et al. (1997) found lower dissolved metal concentrations in a part of the Scheldt estuary (Belgium and The Netherlands) during spring and summer, which were attributed to sulphide formation as a result of the creation of anoxic conditions. Salomons et al. (1987) calculated the influence of the sulphide concentration on the speciation and solubility of Zn, Cu and Cd in a solution with 5000 mg Cl L<sup>-1</sup> and an alkalinity of 50 mmol L<sup>-1</sup>. Effects of chlorides on the solubility of Cd, Cu and Zn and of hydroxides and (bi)carbonates on the solubility of Zn were observed only at low sulphide concentrations (<10<sup>-3</sup> μg L<sup>-1</sup> for Cd, <10<sup>-2</sup> μg L<sup>-1</sup> for Cu and <10<sup>-1</sup> μg L<sup>-1</sup> for Zn), which indeed illustrates the stability of metal sulphide precipitates formed at higher sulphide concentrations. However, at higher sulphide concentrations (>10<sup>5</sup> μg L<sup>-1</sup> for Cd, >10<sup>3</sup> μg L<sup>-1</sup> for Cu and >10 μg L<sup>-1</sup> for Zn), the formation of soluble bi- and polysulphide complexes increased the total metal concentrations in the solution. In pore waters of anoxic environments, (bi)sulphide ions might compete with metals complexed by dissolved organic matter. According to thermodynamical calculations, organic matter does not complex Cu, Zn and Cd to an appreciable extent in the presence of (bi)sulphides (Salomons et al., 1987). No differences in pore water concentrations of sorption experiments were found for Cr and As, whether sulphide was present or not. In both cases, dissolved concentrations could be described by adsorption processes only. Salomons et al. (1987) concluded that Cr and As do not form solid sulphide compounds, which was confirmed by Guo et al. (1997).

Charlatchka and Cambier (2000) studied immobilization of Cd, Pb and Zn in a well-buffered flooded soil. Flooding at first increases Cd, Pb and Zn mobility by decreasing the pH and reducing the Fe and Mn oxides, whereas prolonged flooding periods (>2 months) again lead to immobilisation of these

trace metals, by re-adsorption or precipitation rather than by formation of insoluble sulphides. This was concluded from the observation that sulphides were below  $0.05 \text{ mg L}^{-1}$  in the leachates. Very low sulphide concentrations in the leachates however do not prove the absence of sulphide precipitates in the solid soil fraction as sulphides of Cd, Pb and Zn are highly insoluble. [Salomons et al. \(1987\)](#) reported that the effects of some ligands (e.g., chlorides, hydroxides and bicarbonates) on the metal solubility decrease when sulphide concentrations in solution are increasing and these effects can already disappear when these sulphide concentrations are still very low (e.g.,  $<0.1 \mu\text{g L}^{-1}$ ). Moreover, [Du Laing et al. \(2007b\)](#) calculated that the formation of small sulphide amounts that are below the detection limit of common titration-based analysis procedures could still explain the very low levels of Cd, Cu and Zn amounts in pore water during flooding. [White et al. \(1989\)](#) observed sulphate reduction in the upper sediment layer of a lake, but they did not measure dissolved sulphide concentrations above  $1 \mu\text{mol L}^{-1}$  or  $32 \mu\text{g L}^{-1}$  in solution, which should also be attributed to the low solubility of metal sulphides.

#### 3.4.4. Volatilisation and methylation of mercury

Whereas the above-mentioned processes affect the fate of most metals in floodplain environments, the toxicity, mobility and bioaccumulation of especially mercury (Hg) is also affected to an important extent by some specific processes. The very low redox potentials in permanently or frequently flooded soils and sediments often promote the reduction of Hg(II) to Hg(I) or Hg(0). Mercury may also exist in organometallic forms, of which monomethylmercury ( $\text{CH}_3\text{Hg}^+$ ) and dimethylmercury [ $(\text{CH}_3)_2\text{Hg}$ ] are the most important ([DeLaune et al., 2004, 2008](#); [Devai et al., 2005](#); [Zhong and Wang, 2008](#)). Hg(0) and  $(\text{CH}_3)_2\text{Hg}$ , are volatile species and cause volatilization from soil to atmosphere to be an important pathway for Hg (e.g., [Schroeder and Munthe, 1998](#); [Schroeder et al., 1989](#); [Lin and Pehkonen, 1999](#); [Schlüter, 2000](#); [Böhme et al., 2005](#); [Rinklebe et al., in press](#)). Methylation of mercury is attributed to sulphate reducing bacteria ([Compeau and Bartha, 1987](#)). Sulphate addition can increase methylmercury production ([Jeremiason et al., 2006](#)). The presence of sulphide, however, decreases the availability of  $\text{Hg}^{2+}$  for methylation ([Kongchum et al., 2006](#)). The accumulation of reduced sulphur, primarily as sulphide, causes the precipitation of inorganic Hg in a highly insoluble HgS mineral ([Kaplan et al., 2002](#)). Methylating activity is reported to be lower in marine and estuarine sediments compared to freshwater sediments (e.g., [Blum and Bartha, 1980](#)), which might be attributed to salinity effects ([Kongchum et al., 2006](#)). Monomethylmercury moves up the food chain through several tropic levels ([Davis et al., 1997](#); [Downs et al., 1998](#); [Ullrich et al., 2001](#)). Dimethylmercury [ $(\text{CH}_3)_2\text{Hg}$ ] has less tendency to accumulate because it is a volatile organomercury compound that can escape to the atmosphere ([Manahan, 2000](#)).

#### 3.4.5. Metal fate when reduced sediments are oxidized

Initially reduced sediments can be temporarily or permanently re-oxidized by processes such as ([Gambrell, 1994](#); [Eggleton and Thomas, 2004](#)):

- bioturbation, or the disruption of the integrity of the flooded soil surface through benthic organisms that displace and suspend materials in the surface layer;

- re-suspension due to more turbulent flow conditions (underwater currents, seasonal flooding or storms);
- dredging and land-disposal;
- permanent drainage of wetlands, lowering of the water table level.

Mainly due to the oxidation of sulphides, solubility and leaching of most heavy metals increases when strongly reduced sediments are oxidised ([DeLaune and Smith, 1985](#); [Singh et al., 1998](#)). At a high pH, oxidation of metal sulphides is expected to be purely chemical, whereas it can be microbiologically mediated at much lower pH values ([Salomons et al., 1987](#)). Metals co-precipitated with or adsorbed to FeS and MnS are rapidly oxidised, due to their relative solubility in oxic conditions ([Allen et al., 1993](#); [Simpson et al., 1998](#); [Caetano et al., 2002](#)). However, more stable sulphide-bound metals (such as CuS and pyrite) are unlikely to be oxidized in the short term due to their slower oxidation kinetics ([Caetano et al., 2002](#)). Following sulphide oxidation, the released Fe and Mn can be rapidly re-precipitated and deposited as insoluble oxides/hydroxides, to which newly released metals can become adsorbed at varying rates and extents ([Di Toro et al., 1990](#); [Caetano et al., 2002](#); [Eggleton and Thomas, 2004](#)).

[Tack et al. \(1998\)](#) reported strong metal mobility increases for Cd, Cu, Pb and Zn in oxidised dredged sediments compared to reduced sediments, while leachability of Fe decreases and Mn, Ni and Co were mainly unaffected. [Gambrell et al. \(1991b\)](#) found increasing Cd, Cu, Ni and Zn solubilities upon oxidation of a brackish contaminated sediment at acid and near-neutral pH levels, whereas this was not observed for Cr. Only little Pb mobilization was observed at intermediate redox potentials. [Calmano et al. \(1993\)](#) and [Zoumis et al. \(2001\)](#) reported the binding forms of Cd, Cu, Pb and Zn to change from stronger bound oxidisable fractions to weaker bound carbonate and exchangeable fractions during sediment oxidation, which significantly increased dissolved Cd and Zn concentrations. [Stephens et al. \(2001\)](#) could correlate the leaching patterns of heavy metals in sediments during drying to sulphide:sulphate ratios, which confirmed the role of sulphide oxidation. [van den Berg et al. \(1998a\)](#) also attributed increased metal concentrations in the pore water of a freshwater estuarine soil during summer months to sulphide oxidation as a result of decreasing groundwater levels. [Gerringa et al. \(2001\)](#) reported an increased dissolution of Cd compared to Zn upon oxidative dissolution of Cd and Zn sulphides at high salinities. This was attributed to a combination of the lower solubility of CdS compared to ZnS and the formation of stable Cd chloride complexes with increasing salinities. The formation and re-oxidation of small amounts of sulphides might be dominant in determining total metal concentrations in different profile layers within the intertidal sediments ([Du Laing et al., in press-a](#)) and the mobility of Cd, Cu, and to a lesser extent Zn, in the upper, calcareous soil layer of a contaminated overbank sedimentation zone under alternating hydrological conditions ([Du Laing et al., 2007b](#)). In the latter study, the behaviour of Ni was found to be closely related to the behaviour of Fe and Mn. These effects were strongly dependent on the duration of the flooded periods. The shorter the flooded periods, the better the metal concentrations could be linked to the mobility of Ca in the pore water, which was attributed to a fluctuating  $\text{CO}_2$  pressure.



The increased metal mobility upon oxidation of initially reduced sediments is also reflected in an increased plant availability. Thus, [Vandecasteele et al. \(2005\)](#) found higher Cd concentrations in the leaves and bark of the wetland plant species *Salix cinerea* in the first weeks of the growing season for plots with shorter submersion periods in the field. An upland hydrological regime also resulted in elevated Cd and Zn concentrations for *S. cinerea* and *Populus nigra* in the leaves under greenhouse conditions, compared to a wetland hydrological regime ([Vandecasteele et al., 2007a](#)). Such effect of reducing conditions on metal availability was also reported by others for other plant species ([Gambrell, 1994](#)). Moreover, initially submerged soils emerging only in the second half of the growing season also resulted in elevated Cd and Zn foliar concentrations at the end of the growing season ([Vandecasteele et al., 2005, 2007a](#)).

From the above, it seems important to know whether metal concentrations in the pore water are determined by precipitation–dissolution reactions or by adsorption processes. With precipitation–dissolution processes the concentrations will not depend on the total metal content in the sediment and an increased input in the system will not affect the concentrations in the pore waters. When adsorption is the main process which binds the metals to the sediments, the increased input can cause elevated metal concentrations in pore waters, whereas a decrease in adsorption capacity will also cause an increase in metal levels in the pore waters ([Salomons et al., 1987](#)).

#### 3.4.6. Induced metal fluxes between the oxic and anoxic layer and the oxic–anoxic interface

Calculations using concentration gradients of metals indicate that diffusive fluxes between sediment and surface water contribute to concentrations in the surface water ([van den Berg et al., 1998b](#)). The differences in composition between the oxic and anoxic sediment layers constitute driving forces for the transport of several components. When the oxic–anoxic interface is situated in the floodplain soil or sediment, the composition of the oxic layer will also be changed due to the flux from the anoxic layer. Important in this respect is the enrichment of Fe, Mn and P in the oxic surface layer. This effect and the differences in kinetic parameters between oxidation and reduction reactions determine the transport of components from the anoxic layer to the surface waters ([Salomons et al., 1987](#)). As a result of generally low concentrations of metals in pore waters of anoxic layers, fluxes to oxic layers will be low. However, physical processes such as consolidation and bioturbation can enhance the upward flux. [Simpson et al. \(2002\)](#) studied the effect of tides, bioturbating organisms, and periods of anoxia on metal fluxes from contaminated harbour sediments in a shallow tidal estuarine bay, together with capping technology options for the containment of metal contaminants. More frequent short periods of air exposure followed by renewal of overlying water resulted in a large increase in the Zn flux from the sediments. Moreover, fluxes were found to be greater in the presence of sediment-dwelling organisms. If the organisms were removed, and re-colonizing organisms later added, their bioturbation activities initially lowered Zn fluxes, but fluxes gradually reached steady state at the higher levels seen

previously. Capping materials were found to physically isolate contaminated sediments, provide a binding substrate for metals released from the sediment, and create an anoxic environment below the cap, which stimulates the formation of insoluble metal sulphides. A 5 mm layer of clean sediment was the most effective capping material in reducing Zn fluxes. A 10 mm layer of a zeolite/sand mixture also greatly reduced these fluxes, but significant breakthrough of Zn occurred after 2 weeks, whereas a 20 mm layer of sand was not effective. The presence of organisms disturbed capping materials and increased Zn fluxes again. Finally, [Simpson et al. \(2002\)](#) concluded that capping materials should have a depth of more than 30 cm to minimize organisms burrowing to contaminated sediments beneath.

#### 3.5. Carbonates and pH

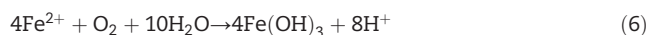
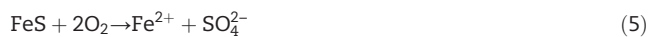
A drop in pH prevents the transfer of most trace metals from the water phase to the floodplain soil or sediment and/or causes a desorption from the soils or sediments (e.g., [Salomons et al., 1987](#); [Gambrell et al., 1991b](#); [Calmano et al., 1993](#)). At low pH, the negative surface charge of organic matter, clay particles and Fe and Al oxides is reduced, and various compounds such as carbonates and sulphides become more soluble. The presence of carbonates in calcareous floodplain soils or sediments constitutes an effective buffer against a decrease in pH. Moreover, carbonates may also directly precipitate metals (e.g., [Gambrell, 1994](#); [Guo et al., 1997](#); [Charlatchka and Cambier, 2000](#)). These carbonates can be geochemically or biogenically formed and deposited as part of the sediments in tidal flats, floodplains or marshes. However, decalcification can also occur and complete decalcification may result in acidification of the pore water. When the pore water reaches a certain pH, heavy metals may rapidly become mobilized. Because decalcification and subsequent mobilization of contaminants are fairly slow in calcareous soils, decalcification of hydric soils is regarded as a chemical time bomb ([van den Berg and Loch, 2000](#)). Not only the pH drop, but also increased Ca concentrations in the pore water during partial decalcification cause an enhanced release of metals in the calcareous soil layer of a contaminated overbank sedimentation zone ([Du Laing et al., 2007b](#)).

Two main causes for decalcification of the top layer of hydric soils are oxidation of Fe sulphides under aerobic conditions and increased CO<sub>2</sub> pressure in the soil during waterlogging. Carbon dioxide is produced in the soil during aerobic breakdown of organic matter, by methanogenesis and by respiration from roots. Diffusion constraints limit the escape of CO<sub>2</sub> to the water column and the atmosphere. Decalcification therefore is more intense in saturated soils (or soil layers) than in aerated soils. Increased CO<sub>2</sub> pressure in the soil results in calcium carbonate dissolution according to:



Vegetation may stimulate decalcification of the soil, especially in the rhizosphere. Both living roots and micro-organisms are sources of CO<sub>2</sub>, and dead roots are a source of easily decomposable organic matter. Oxidation of sulphides may be an important decalcification process in soils subject to

periodic oxidation and reduction. The oxidation of FeS during aeration of the soil can be schematized in two reaction steps:



For each molecule of FeS oxidized, two protons are produced, whereas subsequent precipitation of Fe(III) hydroxides leads to an even higher production of protons. In calcareous soils the decrease in pH is buffered by dissolution of calcium carbonate:



Evidently, the intensity of decalcification due to sulphide oxidation varies with the amount of sulphide formed in the floodplain soil or sediment, and thus on the duration of waterlogging. Depending on the site-specific hydrological conditions, approximately 0.1–0.3% of calcium carbonate may be dissolved per year by a combination of the two processes mentioned above (van den Berg and Loch, 2000).

### 3.6. Plant growth

#### 3.6.1. Metal mobility in the rhizosphere

Wetland plants can oxidise the floodplain soil or sediments in the root zone through movement of oxygen downwards through aerenchyma tissue (Moorhead and Reddy, 1988). This oxidation can remobilize the metal contaminants, thus increasing the availability of metals in wetland soils (Weis and Weis, 2004). Some species of mangroves were found to oxidise the rhizosphere, reducing sulphide contents and enhancing metal concentrations in the exchangeable form (De Lacerda et al., 1993). Wright and Otte (1999) found that *Typha latifolia* oxidised the rhizosphere, but this did not increase pore water metal concentrations. It caused a pH decrease within 1 cm of the roots and it increased the concentration of soluble Zn near and beneath the roots, while another plant, *Glyceria fluitans*, had only little effect on sediment chemistry. A striking feature of roots of some wetland plants is the presence of metal-rich rhizoconcretions or plaque on the roots (Vale et al., 1990). These structures are composed mostly of Fe and Mn hydroxides and other coprecipitated metals, and are often referred to as “iron plaque”. The main element, Fe, could originate from the microbial reduction of Fe oxides in the zone around the roots, the oxidation of Fe sulphides or from  $\text{FeCO}_3$ , which is unstable under oxic conditions (St-Cyr and Crowder, 1988). Together with Fe, other metals are mobilized from the reduced anoxic sediments and concentrated in the oxidized microenvironment around the roots (Doyle and Otte, 1997). Their concentrations can reach 5–10 times the concentrations seen in the surrounding sediments (Sundby et al., 1998). There have been conflicting reports as to whether the presence of the plaque reduces or increases the uptake of metals by the plants (Weis and Weis, 2004). The presence of these concretions appeared to reduce the amount of Zn taken up by *Aster tripolium* (Otte et al., 1989) and the amount of Mn taken up by *Phragmites australis* (Batty et al., 2000). The plaque might have acted as a physical barrier, although the barrier was not effective at low pH conditions. At higher pH conditions the presence of plaque enhanced Cu

uptake into roots. In *T. latifolia* (cattail), the presence of iron plaque did not reduce the uptake of toxic metals (Ye et al., 1998). Iron plaque moreover increased Zn uptake by rice (*Oryza sativa*) and movement into shoots (Zhang et al., 1998).

Metal remobilisation may also result from the excretion of plant exudates (Xu and Jaffe, 2006; Fig. 4). Another factor that can affect the accumulation of metals in wetland plants is the presence of microbial symbionts, such as rhizosphere bacteria. Mycorrhizae, symbiotic fungi associated with roots, can provide an interface between roots and soil, increasing the absorptive surface area of root hairs. They might be effective at assimilating metals that are present at toxic concentrations in the soil, thus restricting metal uptake by the plants. However, they were also reported to increase metal uptake by wetland plants (Weis and Weis, 2004). Moreover, Decho (2000) reported a significant role of extracellular microbial polymeric secretions (microbial biofilms) in intertidal systems, both in the binding and concentration of metal contaminants, as in the trophic transfer of metals to the food web. According to Kunito et al. (2001), these extracellular microbial polymeric secretions were especially produced in large quantities by Cu-resistant bacteria in the rhizosphere of reed plants, which suggest its involvement in the reduction of the bioavailability of Cu.

#### 3.6.2. Metal uptake by plants

Overesch et al. (2007) showed that metal accumulation in floodplain vegetation is element- and plant-specific. They found that As, Cd, Cu, and Hg concentrations in five common plant species of floodplain ecosystems near the Elbe River (Germany) were clearly below maximum values reported for hyperaccumulators (Lasat, 2002), whereas the concentrations of Cu and Pb were also within the range of background levels for plants growing in uncontaminated natural environments (Kabata-Pendias and Pendias, 2001). However, maximum concentrations of Zn in *Artemisia* and *Phalaris* and of Ni in *Alopecurus*, *Agropyron*, *Phalaris* and *Urtica* were at levels which are supposed to be excessive or toxic for plants (Kabata-Pendias and Pendias, 2001). According to Du Laing et al. (in press), the concentrations of metals in reed plants growing in calcareous, intertidal floodplain sediments of the Scheldt estuary (Belgium) are low. They seem to be affected by salinity, organic matter and clay contents. A lower sorption capacity due to a lower clay or organic matter content might decrease the capacity of the sediments to immobilize metals and thus increase the plant availability (see Section 3.1). A lack of organic matter might also hamper the microbial sulphate reduction (see Section 3.4.3). Moreover, less clayey floodplain soils are expected to be susceptible to more rapidly fluctuating water table levels, which lead to occasional oxidation of sulphides and an increased metal availability (Du Laing et al., in press, 2008a).

Large differences between metal and arsenic concentrations of plant species at the same sites were sometimes observed (Overesch et al., 2007). Variable age of biomass, rooting depth, metal mobilization/immobilization by roots in soil, element specific uptake into roots, or transfer into shoots and foliar uptake are factors influencing the behaviour of metals transfer into plants (Kabata-Pendias and Pendias, 2001). For perennial wetland species, metal uptake may be

even more complex. Vandecasteele et al. (2007b) observed clear effects of submersion conditions in previous growing seasons on Cd, Zn and Mn concentrations in leaves and bark of *S. cinerea*, a wetland shrub. Uptake of the essential micronutrients Cu, Ni, and Zn into the root and its transfer into the shoot is often promoted (Welch, 1995). Uptake of the non essential elements As, Cd, Hg, and Pb into roots may be limited or they may be accumulated in roots due to a reduced transfer into the shoot (Kabata-Pendias and Pendias, 2001). These different strategies may explain the frequently low transfer factors of elements such as Cd which are very mobile in the soils, as well as the lower transfer factors of Pb compared to those of Cu, although both revealed a comparable phytoavailability (Overesch et al., 2007).

Redistribution between roots and aerial plant organs, partly influenced by phosphate level of plants, has been discussed as possible mechanism behind seasonal changes of metal concentrations (Matthews and Thornton, 1982). For instance, in some plant species Ni is transferred into seeds during the generative phase and accumulated there (Fismes et al., 2005; Welch, 1995). Cadmium accumulated in tree bark in previous years was transferred to young willow leaves in the first weeks of the growing season (Vandecasteele et al., 2005). Up till now, research of metal fluxes in wetlands mainly focused on plant uptake in permanently submerged or emerged situations (Deng et al., 2004; Qian et al., 1999), while emergence of initially submerged sediments resulted in clear effects on Cd and Zn uptake in *S. cinerea* (Vandecasteele et al., 2005). In the future, more research attention should go to mechanisms of metal transfer from alternately flooded floodplain soils to vegetation, as well as their spatial and temporal dynamics.

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