# Trace metal dynamics in floodplain soils.

## A case study with the river Elbe in Germany

Von der Mathematisch-Naturwissenschaftlichen Fakultät
der Christian-Albrechts-Universität zu Kiel genehmigte

# DISSERTATION

Zur Erlangung des akademischen Grades

DOCTOR RERUM NATURALIUM
(Dr. rer. nat.)

vorgelegt von

Dipl. Geoökologin
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Geboren am 09.04.1977 in Sangerhausen

Kiel, den 23.01.2014

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Tag der mündlichen Prüfung: 06.05.2014

Zum Druck genehmigt, Kiel 06.05.2014

# Acknowledgements

Without the support, patience and guidance of the following people, this study would not have been completed. It is to them that I owe my warm thankfulness.

I would like to express my deep appreciation and gratitude to my advisor, Prof. Dr. Hans-Rudolf Bork, for the patient guidance and mentorship he provided to me, all the way from when I was first considering this PhD through to completion of this work. I thank Prof. Dr. Klaus Henle for supporting this work and giving me the necessary independence working on that topic.

I want to thank Mathias Scholz for selecting me as a trainee some years ago and giving me the possibility to work in several research projects that financed this dissertation. I thank Dr. René Schwartz who first encouraged me carrying out this project.

Many thanks to Prof. Dr. Ralph Meißner and Dr. Holger Rupp for supporting my field work, to Robert Lüdtke for boring wells, sampling soil solution during low and high water levels, keeping the data logger working, storing samples, repairing cables and many funny experiences during the field work, to Karin Muhs for analysing samples and continuous answering my emails with questions about methods, equipment's and procedures in the laboratory, to Frank Krüger an excellent soil scientist without his support I would not have even started the whole work, to Dörthe Betge-Steffens for talking about collective doubts and her groundwater data, to Melitta Stratschka and Juliane Seeger for chatting and making my stays in Falkenberg very cosy.

Many thanks to Prof. Dr. Heinz-Ulrich Neue who hosted me in his department and let me use all the equipment in his laboratory, to Prof. Dr. Jörg Rinklebe for many fruitful discussions in the laboratory and during the interpretation of the data, to Dr. Frank Böhme for giving me beginners and advanced courses in microcosm experiments, to Dr. Elke Schulz for the possibility to work in her laboratory, to Anja During who was a great fellow and friend during that time. I am greatly thankful to Gabriele Henning, Kerstin Hommel, Jaqueline Rose, Martina Stange, Jürgen Steffens, Sibylle Mothes, Hans-Joachim Stärk, Rainer Wennrich, Jutta Fröhlich, Ines Volkmann and Peter Morgenstern for giving me the possibility to work in their laboratories and who analysed many pore water and soil suspension samples for me.

Dr. Bernd Gruber and Dr. Michael Gerisch were able to open my mind for statistics and motivated me to even get into it.

Marlies Uhlig had always comforting words and double-checked the whole document. Sarah Gwillym-Margianto had proofed the English in all the papers.

I am truly appreciating the great working atmosphere at the Department of Conservation Biology at the UFZ in Leipzig and I want to dedicate my thankfulness to past and present colleagues; most of them became my friends. Cheers for NANAWU, coffee breaks, chatting, great

Christmas parties and department trips, the Coimbra experience, crafting days and nights, shooting movies, making books, creating photo albums and many more.

Very special recognition goes out to my family, for their support, encouragement and patience during this journey.

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# Summary

In their natural form river-floodplain-ecosystems are characterised by heterogeneous habitat patterns over a wide range of temporal and spatial scales. Furthermore, due to the connectivity with adjacent rivers they are very dynamic ecosystems driven by fluctuating river water levels. They provide an extraordinary amount of natural resources and are thus recognised as biodiversity hotspots and moreover, they are imperative to humans as they deliver numerous ecosystem functions and services. Attracted by this richness in natural resources, people have been using riverine floodplains for centuries, resulting in a constant exploitation of those ecosystems. Today, riverine floodplains are among the most endangered ecosystems in the world; in Europe and North America more than 90% of them are used by humans and have consequently become functionally extinct. For at least 200 years the impacts of human activities on river-floodplain-ecosystems have been noticeable. Especially with the onset of industrialisation and an increase in population density, rivers were faced with various water quality issues. Trace metals belong to those contaminants that have negative effects on riverine floodplains. Their concentrations in rivers increased markedly in Europe during the 19th and 20th centuries caused mainly by mining and industrial activities but also through sewage discharge, runoff, and atmospheric deposition. Riverine floodplains can take on water quality functions for rivers during periods of flooding due to the ability of floodplain soils to retain pollutants. Consequently, trace metal loads in the water body can be reduced in this way, leaving riverine floodplains heavily polluted with trace metals. Even if river water quality improved considerably over recent decades in Europe, trace metal concentrations in riverine floodplains are still high compared to natural background levels. Due to the high degree of variability in the existing geomorphological forms and the associated biogeochemical characteristics, the frequency and the period of inundation, deposited trace metal concentrations vary in space and time and thus riverine floodplains show high variability regarding diffuse soil contamination. Until now, riverine floodplains have acted as a huge sink for trace metals. However fluctuating seasonal patterns as well as a more frequent occurrence of floods and droughts, that is assumed under the influence of climate change, may influence the physico-chemical as well the biogeochemical conditions in soils that play a major role in controlling the availability, the transport and deposition of sediment and associated trace metals. Thus riverine floodplains can episodically become a source for trace metals as it is widely known that they are already highly sensitive due to small changes in hydrology. Moreover, it is expected that the sensitivity of riverine floodplain components and processes to non-climatic threats such as pollution, is likely to increase as a result of climate change effects.

The study supporting this PhD thesis was conducted within the riverine floodplain 'Schönberg Deich' in the UNSECO Biosphere Reserve 'Riverlandscape Elbe', Germany. This floodplain served as a model region for investigating trace metal dynamics in floodplain soils under seasonal changes in the field as well as using topsoils in the laboratory to simulate strong fluctuating wet-dry cycles. Moreover, results from various research projects along the river Elbe were reviewed. By considering those findings, this thesis pursued the following goals:

(i) Improve the understanding of trace metal dynamics in floodplain soils by providing a deeper knowledge about the spatial and seasonal dependencies of trace metal mobility together with soil biogeochemistry.

(ii) Investigate wet-dry cycles and their impacts on soil biogeochemistry and trace metal dynamics to increase the understanding about possible climate change effects on the retention resp. remobilisation capacity of floodplains.

(iii) Identify combined soil parameters that may explain trace metal behaviour under seasonal changes and a selected climate change scenario as the simulation of wet-dry cycles.

(iv) Interpret the results in conjunction with reviewed literature on general trace metal dynamics compared to data from the river Elbe and its floodplains.

One of the major results found in this PhD thesis was, that dissolved trace metal amounts measured in the field and the laboratory could be assigned to bundles of soil parameters with different statistical significances.

Moreover, in the field, pollution hot spots and hot moments could be identified for different trace metals and throughout the year. Besides, in the laboratory, plot-specific trace metal release patterns were investigated. In both studies trace metal dissolution within the plot that showed the lowest total concentrations was greatest for most of the investigated trace metals. This led to the assumption that this plot in particular might be strongly affected by seasonally shifting hydrology and maybe also due to imminent effects from climate change.

Generally, it could be stated that changing river water levels (resp. anaerobic/aerobic conditions), redox potential, pH-value and spatial characteristics were identified as having a strong influence on trace metal dynamics.

Nevertheless, it is strongly recommended to continue research and monitoring in riverine floodplains with a particular emphasis on identifying multiple factors that could affect trace metal dynamics and singling out effects caused by anthropogenic impacts or by naturally varying factors. Consideration of the potential relationships between anthropogenic threats and climate change in riverine floodplains should be given when planning future management activities and, additionally, this is imperative for an in-depth understanding of trace metal dynamics in riverine floodplains.

# Zusammenfassung

Natürliche und naturnahe Fluss-Auen-Ökosysteme sind charakterisiert durch ein heterogenes Habitatmosaik, das sich über eine weite Spannbreite von zeitlichen und räumlichen Skalen erstreckt. Angetrieben durch beständig schwankende Wasserstände stehen konnektierte Auenbereiche in ständiger Wechselbeziehung mit dem angrenzenden Fluss und stellen somit sehr dynamische Ökosysteme dar. Diese hydrologische Dynamik wie auch das heterogene Habitatmosaik führen dazu, dass Fluss-Auen-Ökosysteme einen außergewöhnlich hohen Anteil an natürlichen Ressourcen bereitstellen. Sie sind als *hot spots* der Biodiversität anerkannt und haben darüber hinaus einen hohen gesellschaftlichen Nutzen für die Bereitstellung zahlreicher Ökosystemfunktionen und –leistungen. Angezogen von der Vielfalt natürlicher Ressourcen werden Fluss-Auen-Ökosysteme seit Jahrhunderten vom Menschen genutzt, was vielfach zu einer konstanten Ausbeutung dieser Ökosysteme geführt hat. Heute gehören sie zu den am meisten gefährdetsten Ökosystemen weltweit. Allein in Europa und Nord Amerika sind 90% aller Fluss-Auen-Ökosysteme anthropogen genutzt, was zu einer stark eingeschränkten Bereitstellung ihrer natürlichen Funktionen geführt hat. Seit ca. 200 Jahren ist der Einfluss menschlicher Nutzung wahrnehmbar. Insbesondere mit dem Beginn der Industrialisierung und dem Anwachsen der Bevölkerungsdichte sind viele Flüsse vielfältigen Verunreinigungen ausgesetzt, welche die Wasserqualität der Flüsse negativ beeinflussen. Spurenmetalle gehören zu den Substanzen, die solche Verunreinigungen hervorrufen können. Hauptsächlich durch Bergbau und industrielle Nutzung während des 19. und 20. Jahrhunderts aber auch durch die Ausbringung von Abwässern, dem Abfluss aus den Einzugsgebieten und atmosphärischer Deposition haben die Spurenmetallkonzentrationen in europäischen Flüssen dramatisch zugenommen. Während Hochwasserereignissen sind die Auenböden in den angrenzenden Auenbereichen in der Lage, Schadstoffe aus dem Flusswasser zu binden und somit eine Reinigungsfunktion für das Flusswasser zu übernehmen. Infolgedessen sind zahlreiche Auenbereiche oftmals stark mit Schadstoffen, darunter Spurenmetallen, belastet. Während sich in den letzten Jahrzehnten der Zustand der europäischen Fließgewässer deutlich verbessert hat, liegen die Gehalte an Spurenmetallen in den angrenzenden Auenbereichen immer noch ein Vielfaches über den natürlichen Hintergrundwerten. Hinzu kommt, dass aufgrund der Verschiedenartigkeit der geomorphologischen Formen und biogeochemischen Charakteristika in Flussauen sowie der davon beeinflussten Überflutungsfrequenz, Flussauen ein räumlich wie auch zeitlich stark variables und somit diffuses Muster an Ablagerungen von Spurenmetallen zeigen. Unter dem Einfluss des prognostizierten Klimawandels und der bestehenden Annahmen über sich verändernde saisonale Muster sowie das vermehrte wechselseitige Auftreten von Hochwasserereignissen und Trockenzeiten ist davon auszugehen, dass sich möglicherweise auch die physikalisch-chemischen sowie die biogeochemischen Eigenschaften der Auenböden,

welche wesentlich die Verfügbarkeit, den Transport und die Ablagerung von Schadstoffen bestimmen, ändern werden. Die Filterfunktion von Auen für Schadstoffe aus den angrenzenden Flüssen könnte dann, betrachtet man die hohe Sensitivität von Auen gegenüber hydrologischen Veränderungen, episodisch zu einer Quellfunktion für gebundene Schadstoffe werden. Darüber hinaus wird angenommen, dass die Sensitivität einzelner Bereiche und Prozesse in Auen gegenüber Belastungen, wie z.B. Verschmutzungen durch Spurenelemente, als Folge der prognostizierten Klimaänderungen möglicherweise stark ansteigen werden.

Die vorliegende Promotionsarbeit wurde im Fluss-Auen-Ökosystem 'Schönberg Deich', das sich im UNESCO Biosphärenreservat ‚Flusslandschaft Elbe' in Deutschland befindet, durchgeführt. Dieser Auenabschnitt entlang der Elbe diente als Modelregion für die vorliegenden Untersuchungen von Spurenmetallen in den Auenböden dreier auentypischer Standorte in Abhängigkeit von saisonalen Veränderungen. Darüber hinaus erfolgten Laborexperimente mit Oberbodenproben dieser Standorte zum Einfluss stark fluktuierender Wasserstände auf die Dynamik von Spurenelementen. Beiden Untersuchungen ging eine Literaturrecherche voraus, in welcher Daten zur Dynamik von Spurenmetallen in Auenböden und speziell in Auen entlang der Elbe zusammengestellt wurden. Diese Studien zugrunde legend verfolgte die vorliegende Arbeit folgende Ziele:

(i) Die Fortschreibung des Wissens über die Dynamik von Spurenelementen in Auenböden durch die Bereitstellung von Felddaten zur räumlichen und zeitlichen Abhängigkeit von Spurenelementen zusammen mit Daten zu biogeochemischen Eigenschaften von Auenböden.

(ii) Die Untersuchung von simulierten, aufeinanderfolgenden Nass- und Trockenzeiten und deren Auswirkungen auf die biogeochemischen Eigenschaften und die Dynamik von Spurenelementen in Auenböden zum besseren Verständnis der Retentions- bzw. Remobilisierungskapazität von Auenböden für Spurenelemente.

(iii) Die Identifizierung von Kombinationen von Bodenparametern, welche die Dynamik von Spurenelementen in Auenböden unter saisonal schwankenden Bedingungen sowie in simulierten Laborexperimenten beschreiben.

(iv) Die Interpretation der Ergebnisse in Zusammenhang mit der bereits bestehenden Literatur zur Dynamik von Spurenelementen in Auenböden, speziell entlang der Elbe.

In den Feld- wie auch den Laboruntersuchungen konnte festgestellt werden, dass jeweils verschiedene Bodeneigenschaften, zu unterschiedlichen Anteilen, die Menge der gelöst vorliegenden Spurenelemente beeinflussen. Darüber hinaus konnten im Gelände räumliche und zeitliche Belastungsschwerpunkte für verschiedene Spurenelemente identifiziert werden, die durch die ermittelten standortspezifischen Freisetzungsmuster für die untersuchten

Spurenelemente im Labor Bestätigung fanden. In beiden Studien zeigte der Standort mit der geringsten totalen Spurenmetallbelastung im Boden für die meisten untersuchten Metalle die höchsten gemessenen gelösten Anteile. Das führt zu der Annahme, dass dieser Standort vermutlich stärker durch wechselnde hydrologische Gegebenheiten und womöglich auch von den zu erwartenden Klimaänderungen betroffen sein wird, als die anderen untersuchten Standorte.

Schwankende Wasserstände und der Wechsel von anaeroben/aeroben Bedingungen im Boden und damit in Zusammenhang stehende wechselnde Redoxbedingungen und pH-Werte sowie räumliche Standortunterschiede konnten als wichtige Kriterien für sich ändernde Spurenmetalldynamiken identifiziert werden.

Zusammengefasst lässt sich aus den Ergebnissen ableiten, dass die Fortsetzung von Forschungsarbeiten und Monitoring-Programmen insbesondere zur Identifizierung von mehreren nebeneinander wirkenden Faktoren auf die Dynamik von Spurenmetallen sowie zur Identifizierung von anthropogen bzw. natürlich beeinflussten Effekten in Fluss-Auen-Ökosystemen zu empfehlen ist. Dabei sind mögliche Wechselwirkungen zwischen anthropogenen Beeinflussungen und klimatischen Veränderungen bei der Planung zukünftiger Management-Programme einzubeziehen, insbesondere da diese für ein gründliches Verständnis der Dynamik von Spurenelementen in Fluss-Auen-Ökosystemen unerlässlich sind.

Chapter 1

# General introduction

## 1.1 Background

### 1.1.1 The formation of rivers and their floodplains

Rivers owe their existence, and are strongly influenced by, tectonic activities as well as climatic variability, including erosion and sedimentation processes due to hydrological variability (Gibbard 1988, Rohdenburg 1989). Tectonically important for Europe were two major influences: the fragmentation of the Eurasian-North American plate, and the Alpine orogenesis that resulted in a great complexity of both structural and depositional patterns. Climatically, the fluvial-geomorphological processes during the glacial and interglacial periods are crucial for the morphological appearance of rivers and their floodplains (Leser 2003). Three basic types of floodplains were identified: (i) disequilibrium floodplains (high energy, non-cohesive), (ii) equilibrium floodplains (medium energy, non-cohesive), and (iii) low-gradient floodplains (low energy, cohesive). Disequilibrium floodplains erode following extreme episodic flow events and tend to be located in steep headwaters. Here, channel migration is restricted by coarse substrate and narrow valleys. Floodplains are mainly constructed by vertical accretion and leading landforms are boulder levees, sand and gravel slopes, and back channels and scour holes. Equilibrium floodplains are formed during regular flow events in broad valleys. It is assumed that these floodplains are in dynamic equilibrium with the flow regime. Fluvial energy from extreme floods tops the channel banks and spreads across an expansive surface. Lateral point bar or braid channel growth are included in the floodplain construction. Channels can be braided, anastomosed or meandering. Typical landforms include abandoned channels, bars and islands, oxbows, meander loops and backswamps. Low-gradient floodplains are also formed by regular flow events in broad valleys. However, here channels are laterally stabilised by erosion-resistant banks of fine cohesive alluvium. Due to the vertical deposition of fine sediment and the occasional channel avulsion, floodplains are normally formed (cf. Ward et al. 2002). The channels themselves are distinguished in (i) extremely narrow, deep and branchless, (ii) narrow, deep, branchless but meandering, and (iii) broad, shallow and braided (Rohdenburg 1989).

### 1.1.2 Riverine floodplain ecosystems

Floodplains are “low-relief Earth surfaces composed of fluvial deposits, and positioned adjacent to river channels” (Tockner et al. 2010, cited according to Naiman et al. 2005 and Stanford et al. 2005). According to the Ramsar Classification for Wetland Types (2012) the term floodplain is a broad term referring to one or more wetland types, including e.g. seasonally inundated grasslands (including natural wet meadows), shrub lands, woodlands and forests. Riverine floodplains are primarily fed from the lateral overflow of river water but also from groundwater, upland sources and direct precipitation (Tockner and Stanford 2002). These areas are usually defined as eco-tones between terrestrial and aquatic territories influenced by fluctuating groundwater tables or extreme floods. Hydrological connectivity is a key process in riverine areas since it refers to the water-mediated transfer of energy, matter and organisms within and among the features of river-floodplain ecosystems (cf. Tockner and Stanford 2002). The development of floodplains is mainly driven by the flood pulse concept (FPC) with its recent extensions and derivatives (Junk et al. 1989, Tockner et al. 2000, Junk and Wantzen 2004, Thorp et al. 2006) and by the shifting habitat mosaic concept (SHM) (e.g. Stanford et al. 2005). The FPC underlines the pulsing of river discharge as the major driving force that determines the degree of connectivity and the exchange of matter across river-floodplain gradients, whereas the SHM identifies that the interaction of physical and biotic processes in floodplains leads to continually changing spatial patterns of habitats favouring high biodiversity. Natural floodplains are: "amongst the most dynamic and heterogeneous ecosystems with complex patterns of variation over a wide range of temporal and spatial scales" (Tockner et al. 2010). Since biological communities are formed and ecosystem processes are restricted by all factors that are critical, on a global scale floodplains provide an extraordinary amount of unique and important ecosystem functions and services, including supplying water, reducing flood risks, maintaining base flows, retaining sediments and binding substances; acting as local hot spots of biodiversity, sequestering carbon, providing food and recreation facilities etc. (e.g. Costanza et al. 1997, Tockner and Stanford 2002, Hannson et al. 2005, Zedler and Kercher 2005).

### 1.1.3 Floodplain soils

According to the KA5 (AG Boden 2005) alluvial soils[1] belong to semi-terrestric soils, whereby the soil formation and the influence of the groundwater table are unified. The alluvial soils class encompasses soils from Holocene fluvial sediments in stream and riverbeds. These soils are periodically to episodically flooded or have been flooded in the past. Usually they have greatly fluctuating groundwater levels that are typically connected to the nearby river water level. The fluctuating amplitude reaches the topsoils and decreases with the distance to the adjacent river. Alluvial sediments consist of (i) deposited, more or less humus material that is usually from the topsoil, (ii) mixtures of different materials from different horizons of eroded soils and (iii) less or non-weathered loose rocks. Very often topsoils (Ah-horizons) are covered and visible stratifications occur within the soil profile. Types of alluvial soils are: *Rambla, Paternia, Kalkpaternia, Tschernitza* and *Vega.* According to the IUSS/ISRIC/FAO (2006) alluvial soils are named as Fluvisols (FL) that can further be qualified by prefix qualifiers comprising those that are typically associated with the reference soil group and suffix qualifiers that relate to (i) diagnostic horizons, properties or materials; (ii) chemical characteristics; (iii) physical

[1] Alluvial soils and floodplain soils are synonymous used

characteristics; (iv) mineralogical characteristics; (v) surface characteristics; (vi) textural characteristics, including coarse fragments; (vii) colour and (viii) remaining qualifiers.

### 1.1.4 Anthropogenic impacts on riverine floodplain ecosystems

Due to their unique semi-terrestrial position, floodplains are remarkably sensitive systems; slight alterations in flow, temperature and landscape composition can already have major and sometimes even irreversible consequences on ecosystem processes and biodiversity (cf. Tockner et al. 2010). Because of the provision of various ecosystem services, riverine floodplains were very attractive for people to exploit (Verhoeven and Setter 2010). Today, they are among the most endangered ecosystems in the world. In Europe and North America more than 90% of riverine floodplains are used by humans and have thus become functionally extinct (Tockner and Stanford 2002). Consequently, today they need to be distinguished as active (regularly flooded by river water) or inactive (separated by a dyke from river water flooding) which indicates the loss of floodplain area. As hydrology is identified as the single most important driving variable in riverine floodplains (Erwin 2009, Keddy 2010), changes in the river flow can alter the extent, duration and frequency of their inundation most profoundly. Those changes often occur from water extraction, dam construction, drainage, or river control and mostly end up by dis-connecting rivers from their adjacent floodplains (cf. Moss and Monstadt 2008). Consequently, key functions such as biodiversity support, flood mitigation, carbon storage and water quality improvement (Zedler and Kercher 2005) are negatively affected by disturbed hydrological processes. In addition, rivers and their floodplains face dramatic problems in terms of significantly decreasing freshwater biodiversity due to modified habitats that are mostly caused by changing land use patterns and intensive, mostly, arable land uses in their catchments, the increase in invasive species and also due to pollution (Tockner and Stanford 2002).

### 1.1.5 Trace metals in floodplain soils

For at least 200 years the impacts of human activities on river systems have been noticeable. Since the beginning of industrialisation and an increase in population density, rivers have faced several water quality problems. Trace metal concentrations in rivers increased markedly in Europe during the 19th and 20th centuries caused mainly by mining and industrial activities but also from sewage discharge, runoff, and atmospheric deposition. Since surface water concentrations of trace metals reached alarming proportions in the 1970s, regulations were implemented to control trace metal release at the source. As far as trace metals are concerned, riverine floodplains can adopt water quality functions for rivers during periods of flooding. As trace metals are mainly bound to sediments, overbank flooding is the major pathway for diffuse trace metal pollution into floodplain soils (Zerling et al. 2006). Consequently, trace metal loads in the water body are reduced whereas riverine floodplains are usually heavily polluted with trace metals (Middelkoop 2000, Schwartz 2001, Eisenmann 2002, Hobbelen et al. 2004, Krueger and Groengroeft 2004). Due to the fact that floodplains display strong spatial as well as seasonal heterogeneity they can be both sinks and sources for trace metals (Eisenmann 2002). Whereas the pollutant retention function is very well known (e.g. Hobbelen et al. 2004, Krueger and Groengroeft 2004, Ciszewski et al. 2008) there are only a few studies that investigate the release of trace metals from floodplain soils under field conditions (e.g. Dong et al. 2005, Van Griethuysen et al. 2005, Graf et al. 2007, Lair et al. 2008). In fact, it is mainly from laboratory studies that we are aware of how changes in soil biogeochemistry lead to trace metal release from floodplain soils; redox processes that take place in combination with pH-value changes are the most important factors for retention and remobilisation triggered by hydrological conditions within floodplains and across river-floodplain gradients (Schulz-Zunkel and Krueger 2009). However, as long as redox processes and pH are affected they will be accompanied by the oxidation and the reduction of iron (Fe) and manganese (Mn), changes in S-cycling, the presence of complex agents such as dissolved organic carbon (DOC) as well as fluctuating microbial activity. This becomes very relevant since even small changes in the frequency, magnitude and timing of e.g. drying and rewetting possibly resulting from climate change can result in large shifts in the net ecosystem exchange, making floodplains a periodic source of matter including trace metals (Tockner et al. 2010). At the same time the PRESS-report (Maes et al. 2012) highlights the potential of wetlands, rivers, streams, and lakes for removing or immobilising pollutants and providing clean water for multiple uses, lowering the cost of wastewater treatment that is based solely on technological solutions. And yet, the quantification of metal mobilisation on the basis of changing biogeochemical conditions is still lacking. Furthermore, the total content of trace metals in soils does not provide sufficient information about potential environmental risks (Joubert et al. 2007). For this reason, investigating trace metals in the soil solution or the soil suspension is essential to describe contaminant bioavailability and toxicity. However, to understand the fate of trace metals in floodplain soils, complex interactions between nutrients, hydrology and pollutant levels need to be described and yet only little is known about the fate and dynamics of dissolved trace metals and those factors determining trace metal dissolution in spatially and seasonally variable freshwater environments, especially under climate-induced changes e.g. wet-dry cycles. Moreover, dissolved amounts of trace metals alone still do not indicate to which amount they will be transported to water bodies, food chains etc. and consequently the eco-toxicological effect of possible metal release is still very uncertain.

### 1.1.6 Climate change and riverine floodplain ecosystems

Another threat to riverine floodplains is the predicted climate change; mainly its impact on water availability and hydrological risks. However, its impacts on water quality are just starting to be studied (Delpla et al. 2009) even if one is aware that even small changes to the hydrology of riverine floodplains can episodically become a matter source (Tockner et al. 2010), which can include trace metals. Climate change impacts are manifold and may influence riparian ecosystems at several scales, spatially and temporally; e.g. the sensitivity of riparian hydrological regimes to climate change may result in seasonal changes of flow, as well as volume (cf. Capon et al. 2013). Furthermore, it has been proposed that strong fluctuations between floods and droughts will occur more frequently under the influence of climate change (EEA 2012). Such changes may influence the physico-chemical as well as the biogeochemical conditions in soils, which control the availability (Poot et al. 2007), the transport and deposition of sediment and associated trace metals (Thonon et al. 2006). Moreover, fluvial and upland geomorphic processes are also main factors concerning physical and biogeochemical patterns and processes in riparian ecosystems (Gregory et al. 1991) and are likewise sensitive to projected climate change. Moreover, hydrological changes are expected to have serious effects on the channel forms and fluvial dynamics of rivers and their riparian areas as a result of fluctuating sedimentation processes (Nearing et al. 2004). As trace metals mainly bind with sediments, especially in fine-grained alluvial soils, such effects may also affect trace metal inputs in floodplains.

## 1.2 Aims and scope of the thesis

Since ancient times floodplains have been intensively used resulting in mainly altered and less functioning ecosystems. Trace metal pollution is one major anthropogenic threat to them, negatively influencing ecosystem functions and services, especially river water quality. Moreover, trace metal pollution acts on several scales within river-floodplain ecosystems impacting on e.g. plant uptake and food chains, erosion and sedimentation processes as well as the trace metal load transported within the river, thus affecting the entire river catchment area as well as the ocean. Additionally, trace metal dynamics are strongly associated with changing climate conditions and thus with e.g. changing hydrological regimes, sedimentation processes etc. Thus the sensitivity of riparian ecosystem components and processes to non-climatic threats is likely to grow as a result of climate change effects. Feedback loops of this kind may amplify anthropogenic effects on riparian ecological dynamics and biodiversity more rapidly in the future, and are likely to increase the effects of synergies among multiple stressors (cf. Capon et al. 2013). Floodplains currently act as a huge sink for trace metals. However, physical and biogeochemical processes in floodplain soils that are mainly responsible for retaining contaminants are very diverse and it is not only a single process alone that should be related to matter dynamics. Moreover, it is still unclear under which circumstances floodplains may also act as sources for pollutants. Thus, the central aim of this thesis is to improve the understanding of trace metal dynamics in floodplain soils by providing deeper knowledge about spatial and seasonal dependencies of trace metal mobility together with soil biogeochemistry. In addition, the investigation of wet-dry cycles and their impacts on soil biogeochemistry and trace metal dynamics should provide a better understanding about possible climate change effects on the retention resp. remobilisation capacity of floodplains. Both questions are related to combined bundles of soil parameters that may explain trace metal behaviour under such circumstances. These results are reflected and interpreted together with reviewed literature on trace metal dynamics in general, with data from the river Elbe and its floodplains. The overall background of the investigations is to contribute and provide useful information to maintain, re-store and manage river-floodplain ecosystems (Fig. 1.1).

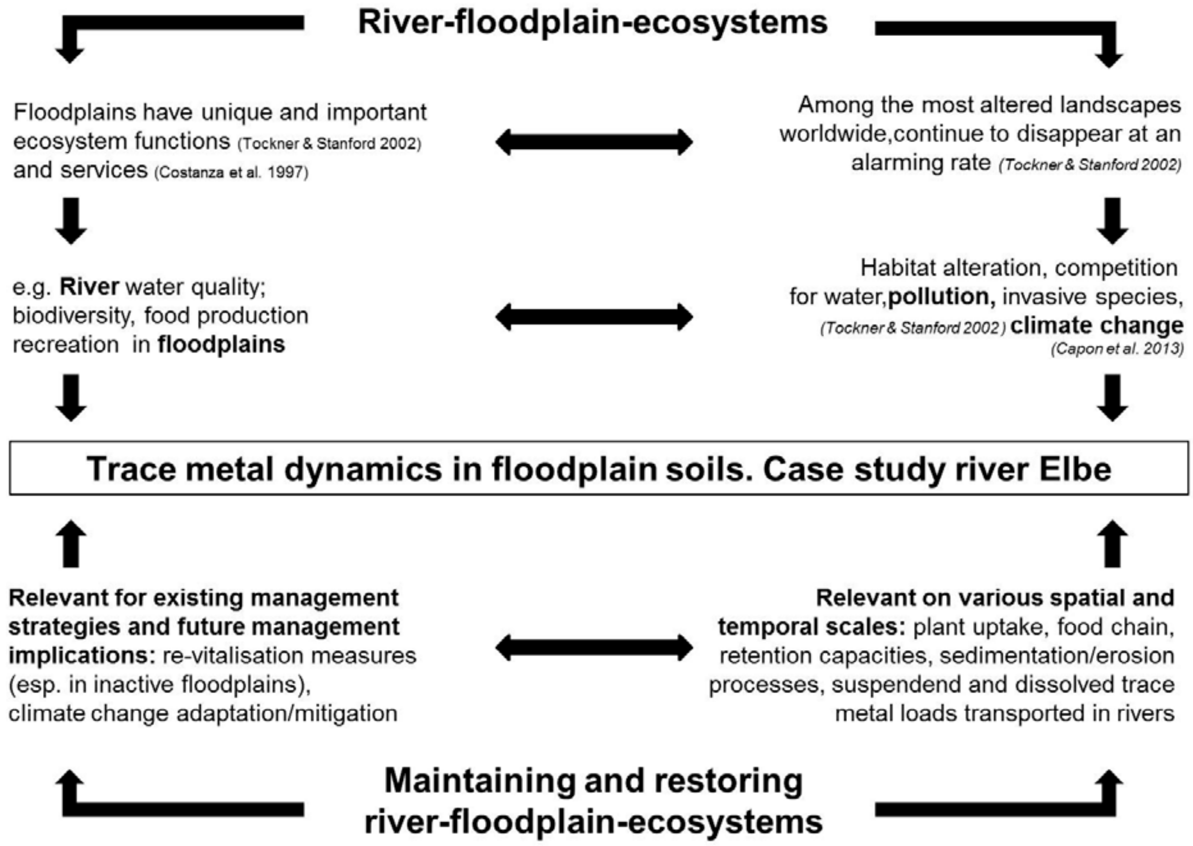


Figure 1.1 Thesis contributions to the research of trace metal dynamics in floodplain soils

## 1.3 Research area and studied plots

### 1.3.1 The river Elbe and its floodplains

The first signs of an ancient Elbe exist from the Tertiary period. During this time a widely branched river system drained the river catchment area and entered the sea north-east of Dresden. The geomorphological character of the river Elbe today was mainly shaped during the cold periods of the Quaternary: Elsterian glacial stage, Saale glacial stage, Weichselian glacial stage. During the Elsterian and Saale glacial period thick sediment layers were deposited. With the onset of the Weichselian stage great vertical erosion, within the present-day Elbe course, into older Pleistocene deposits took place and sand layers up to 15m thick were accumulated. By the end of the Weichselian stage and the beginning of the Holocene backward vertical erosion started from the lower course of the river Elbe. As a result, out of the Weichselian sediments the lower terrace morphologically evolved. Ongoing erosion and sedimentation during the Atlantic stage led to the deposition of thick Holocene terraces. During the Subboreal and Subatlantic stages alluvial loams were sedimented and overlayed the Holocene terraces. These sedimentation areas with cover-building alluvial loams, the occurrence of thick sand layers and drifting sands formed the existing river floodplains which were reduced in their extent by embankments from the beginning of the 1100 AD onwards (cf. Eisenmann 2002).

Figure 1.2 The river Elbe along the floodplain ‘Schönberg Deich‘ (Source: C. Schulz-Zunkel)

The German river Elbe is divided into three sections: the Upper Elbe, the Middle Elbe and the Lower Elbe (IKSE 1995). Nowadays, the river Elbe is the third largest river in Central Europe, in terms of its length and the size of its catchment area. Its discharge is mainly influenced by snow melt in spring and thus high water levels mainly occur in spring. The river Elbe, its floodplains and the catchment area also faced long periods of settlement that led to transformations of floodplains into arable land. Together with this development dykes were built and as early as 1823 76% of the total inundation area was cut off from direct flooding through river water. Over the last 250 years the tide-independent Elbe has been shortened by about 20km (3.2%) and any further evolving of the course of the river has nearly completely stopped. By the end of the 18$^{th}$ century almost all Elbe islands had been removed (cf. Rommel 2000). Nowadays, notable landscape differences exist between the active and inactive floodplains, with the latter mainly used for intensive agricultural production and the active floodplains, that are mostly grasslands, are extensively used as meadows, pastures or both (Scholten et al. 2005). However, as far as its process dynamics are concerned the river Elbe in Germany and its remaining active floodplains have remained semi-natural (e.g. Fig. 1.2). Channelling has not taken place and only a few meanders have been straightened. It has however lost a majority of its floodplains. Those that do actually remain are regularly flooded and thus are able to maintain the wetland and floodplain forest habitats that are unique within central Europe (cf. Adams et al. 2001). Due to these unique features of the natural environment, most parts of the river Elbe and its floodplains have been protected since 1997 as the UNSECO Biosphere Reserve ‘Riverlandscape Elbe’ with a size of about 343.000 ha. This is the biggest inland Biosphere Reserve in Germany and represents one of the last near-natural river landscapes of Central Europe (Fig. 1.3). It stretches for a 400 kilometre long section along the Middle Elbe and encompasses various typical river and floodplain structures embedded in a century-old cultural landscape. To conserve and further protect this landscape several floodplain re-vitalisation projects are in planning or have already been started following the Initiative Flood Prevention Action Plan for the Elbe (IKSE 2003). One main aspect is the improvement of the potential of ecological flood protection. However, several constraints (hydrological, geomorphological and biogeochemical) have to be considered in combination with floodplain re-vitalisation, water conservation and the conservation and development of wetlands (Lamers et al. 2006). Biogeochemical constraints are of major importance for the river Elbe and especially its floodplains; in 1989 the river Elbe was one of the most polluted rivers in Europe due to intensive industrial and agricultural production within its catchment area (Scholten et al. 2005). Even if the river water of the river Elbe over the past twenty years has been notably improved, suspended matter and sediments are still contaminated with trace metals and most of those concentrations exceed the given threshold values according to the German Soil Protection Guideline (BBodSchV 1999) (Krueger et al. 2005). In addition, trace metal concentrations in the German Elbe floodplains greatly vary (Krueger and Groengroeft 2004) and thus make general assumptions for maintaining or improving river water quality and floodplain management or re-vitalisation projects rather complicated.


Figure 1.3 Biosphere Reserve ‚Elbe River Landscape‘
(Source: Biosphere Reserve ‚Elbe River Landscape‘)

### 1.3.2 The Middle Elbe research area and its floodplain soils

The development of alluvial soils within the Middle Elbe region is a result of manifold geological and pedological processes as well as anthropogenic transformations. Sedimentation processes were mainly determined by fluctuating river water levels until the beginning of the Holocene. These led to the formation of levees made from Holocene sands and situated parallel and close to rivers, especially along the lower Middle Elbe. Moreover, finer particles were deposited at greater distances from the river where flow velocities were low. With the beginning of industrialisation and population growth in the early and late middle ages most of the alluvial forests were cleared throughout the whole Elbe catchment. Following especially intensive rainfall, massive erosion took place leading to increased sediment transport and deposition within floodplains. As a result the Holocene sands were overlaid by small-sized particles and less humic material, the so called alluvial loam that covers most of the Elbe floodplains today.

With increasing groundwater levels in the floodplains, muds and peats developed. Due to continuous dynamic flood events that still exist today and thus shifts of the river and its branches several alluvial sediments were characterised by alternating layers of sand and loam. Especially recently deposited sediments contain higher organic carbon and also pollutants, including trace metals. The soil formation in floodplains is characterised by several dynamic processes such as flood-induced erosion and sedimentation as well as the river-water level dependent reduction, oxidation and transport of iron and manganese within the soil profile. The initial substrate of the pedogenesis was postglacial sands, deposited alluvial loam as well as recently deposited alluvial sands and alluvial mud (cf. Scholz et al. 2005).

### 1.3.3 The 'Schönberg Deich' floodplain

All investigations were carried out within the floodplain 'Schönberg Deich'. This area was already used as a model area for former research projects and thus provided useful information. It is an active floodplain situated on the west of the lower Middle Elbe between stream-km 435 to 440 within a meander loop that encloses an area of ca. 200 ha. Referring to the long-term average, the area is situated in a sub-humid climate. The investigations were carried out on plots that are part of a longer transect. Figure 1.4 shows the 'Schönberg Deich' transect including the studied plots from the riparian zone through the floodplain to the dyke. Moreover, this sequence shows a typical order of the different substrates and the relative position to the mean water level of the river Elbe. Dependent on those characteristics different soil types can be identified in floodplains; within the narrow riparian zone ca. 1.5m below the mean river water level, raw soils are dominant that belong to the sub-hydric soils. Here only annual vegetation persists. Still within but in the broader riparian zone, ca. 1-2m above the mean river water level, the soil type Rambla is characteristic. Depending on the duration of humus enrichment, a Paternia may also evolve. This Rambla-Paternia zone is the typical habitat of softwood forests. At sites higher than 3m above the mean river-water level (levee, plateau), that is only flooded during a few days of the year, terrestrial soil formation processes occur. Here the Vega dominates and usually hardword forests find their optimal habitat. At such elevated sites ox-bow channels or depressions exist. They are normally situated ca. 0.5m above the mean river water level with hydromorphic soil profile characteristics dominating. Thus mainly gleyic soil types occur (alluvial gley, wet gley, anmoor gley). Moreover, due to the fact that within those areas flow velocities are very low, they can have large amounts of up to 95% of fine particles (clay, silt) (cf. Scholz et al. 2005). In terms of trace metal input and sequestration the latter ones are usually heavily polluted. The 'Schönberg Deich' area is dominated by grasslands and used, including the groyne fields, as meadows and for cattle grazing with different usage intensities (Rupp et al. 2000). The area is flooded regularly in spring, and due to a diverse micro-topography the whole area is flooded during higher flood events. Within the study area we identified three study plots that are typical hydro-geomorphological structures within floodplains: levee, plateau and depression. Those plots represent a topographical as well as a pollution gradient from slightly (levee) via medium (plateau) to high (depression) flooding frequencies, flood duration and total trace metal content. Additionally, the studied plots show different communities of plants; levee: ash-elm floodplain hardwood forest *(Fraxinoexcelsioris Ulmetum),* depression: red beds *(Phalaridetum arundinaceae),* plateau*:* meadow foxtail grassland *(Alopecuretum pratensis).*

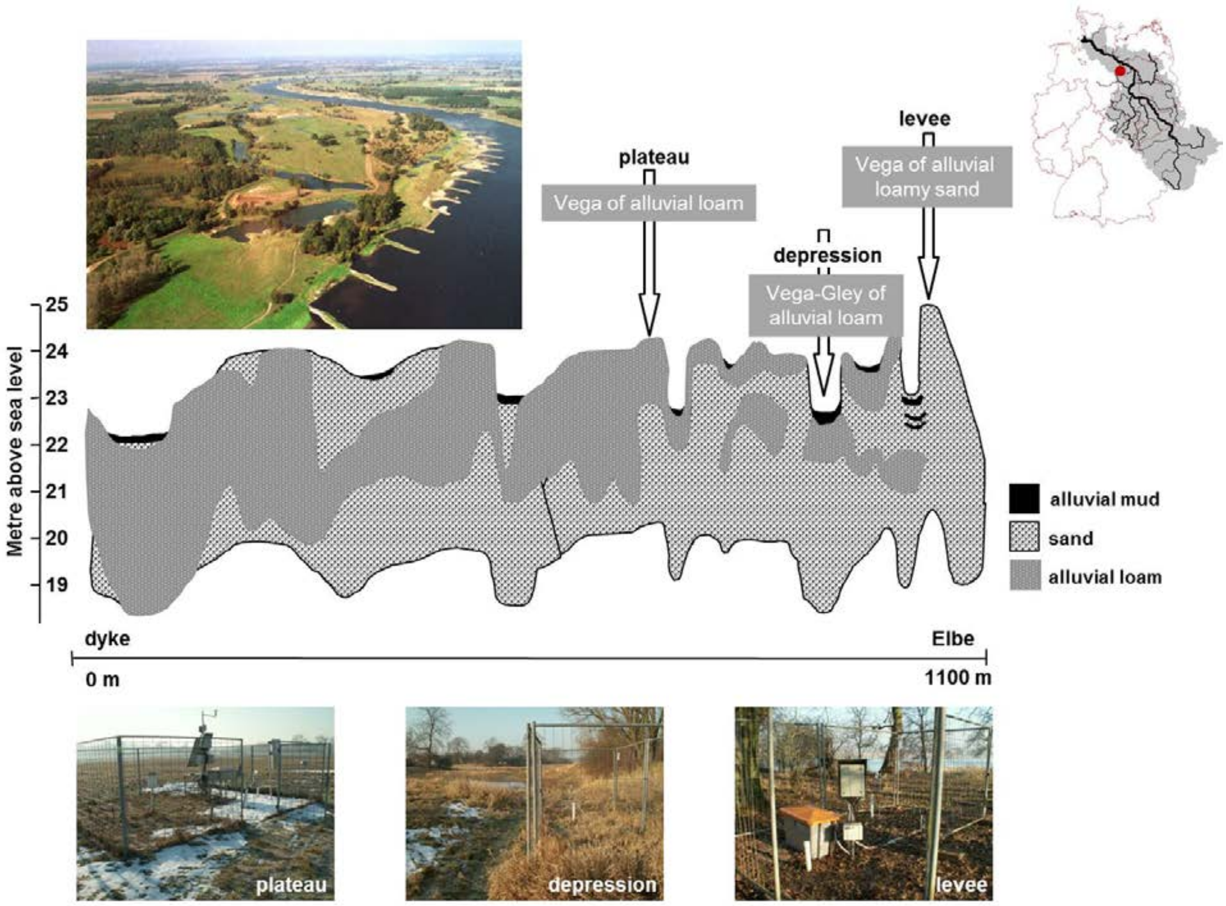


Figure 1.4 The floodplain 'Schönberg Deich' and a segment of its profile including the location of the studied plots (adapted from Krueger et al. 2004a)

### 1.3.4 Data sampling

***Field measurements***

For the field studies we installed field-monitoring stations at all three plots to observe soil parameters and to indicate biogeochemical changes within the soil solution. We installed sensors at three different depths; four within the plateau plot for measuring volumetric soil moisture content (F), redox potential ($E_H$) as well as soil temperature (T). We used five repetitions for the redox potential measurements on the levee and the depression plot and three repetitions on the plateau plot. For temperature and soil moisture measurements we only used one sensor per horizon. Data were monitored daily every full hour by using a data logger. In addition to that, we installed suction cups for collecting soil solution samples (Fig. 1.5). The suction cups were installed in three repetitions for all plots. Under high water levels (surface and/or groundwater) soil solution samples were taken at all depths once a week, resp. during floods every day. We analysed the soil solution samples for dissolved organic carbon (DOC), the trace metals arsenic (As), cadmium (Cd), copper (Cu), chromium (Cr), nickel (Ni) and zinc (Zn) as well as for iron (Fe), manganese (Mn), nitrate-nitrogen ($NO_3$-N) and sulphate ($SO_4^{2-}$), and for pH-value. For all horizons we took soil samples and analysed them for total carbon (C) and nitrogen (N), pH-value and total trace metal concentrations after aqua regia dissolution. In addition we used river water levels at the Wittenberge gauge. Data were sampled from July 2005 until August 2008.

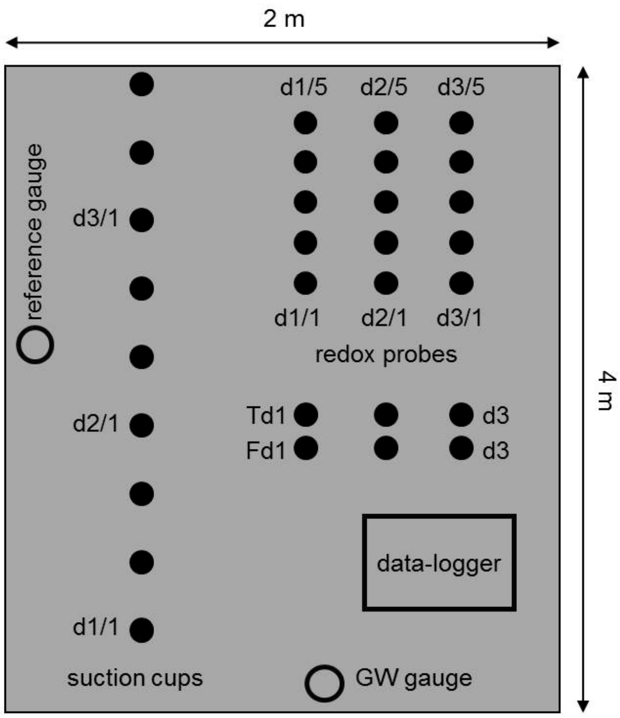


Figure 1.5 Description of the field monitoring stations
*(d1-d3=depth 1 to 3, d1/1=first repetition in depth 1, Td1= temperature at depth1, Fd1=soil moisture at depth 1, GW=groundwater)*

***Experimental set-up in the laboratory***

For the laboratory studies we took horizon-specific samples from the Ah- (levee, depression) resp. the aMAh-horizon (plateau). Since the laboratory investigations were carried out in three replicates, soil material was collected with the aim of pooling these to one composite sample for each horizon. Soil material was homogenised, air-dried and sieved <2 mm. Soil samples were analysed for total C and N, particle-size distribution, pH-value and total trace metal concentrations (As, Cd, Cu, Cr, Ni, Zn) after an aqua regia dissolution. For the microcosm setup, three replicates of each soil were incubated (soil–water ratio: 1:8) in the biogeochemical microcosms. A platinum electrode with a silver–silver chloride reference electrode was used for the redox measurement ($E_H$) whereas a pH electrode was utilized for the pH-value measurement. $E_H$ and pH in the soil suspension of each microcosm were automatically monitored every 10 min. Data recorded by the sensors were collected by a data logger. The simulation of the two succeeding cycles from aerobic to anaerobic conditions was created by adding nitrate (to reach lower $E_H$) and oxygen (to rise $E_H$) from an automatic valve-gas regulation system. The experiment lasted for 85 days. We took nine soil suspension samples during the experiment at defined $E_H$ levels.

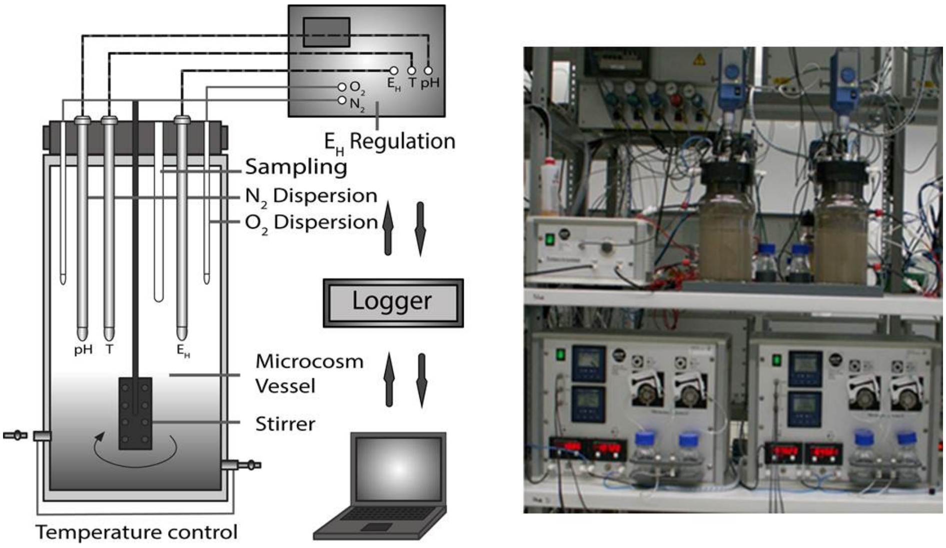


Figure 1.6 Soil microcosm set-up (adapted from: Rupp et al. 2010)

## 1.4 Structure of the thesis

This thesis comprises five chapters. This first chapter introduces the background, the aims and the methodology of the study. Chapter's two to four present the results of the research that was conducted, written in the form of scientific papers. Chapter five completes the thesis by providing a synopsis of the main findings and reflecting on the reviewed studies, the field investigations, the simulation experiment in the laboratory as well as considering general assumptions and possible impacts on future management strategies in floodplains in terms of conserving, enhancing and recovering the multifunctionality of floodplains. In the following, I will give a brief overview of the aims and relevance of the research chapters.

***Chapter 2***

This chapter reviews the existing literature on the pollution and fate of trace metals in rivers and their floodplains depending on physico-chemical and biogeochemical processes. General findings are reflected using data from the river Elbe floodplains. The information encompasses laboratory and field investigations and provides general assumptions concerning factors affecting the mobility and availability of the most important trace metals in floodplain soils, including the river Elbe floodplains. This chapter gives a broad introduction to the topic of trace metal dynamics in floodplain soils but also the limitations of field and laboratory investigations to describe and especially quantify trace metal availability in floodplain soils. This is of crucial importance since especially bioavailable trace metals affect several aspects of floodplains that are important to human well-being such as the provision of drinking water and food production. Therefore, this chapter also reveal existing knowledge gaps and further research needs.

***Chapter 3***

Chapter 3 provide data from monitoring the seasonal and spatial distribution of trace metals in floodplain soils targeting to reduce existing limitations particular in field investigations on trace metal dynamics in floodplain soils related to multiple physico-chemical and biogeochemical processes. Trace metal and soil data as well as river water levels were collected over a three-year period. The main aim of this chapter is to recognise differences between the three investigated plots with respect to the total trace metal content but also, and most importantly, to the dissolved trace metal content in the soil solution during changing river water levels. In addition, we identified hot spots and hot moments of dissolved trace metals and were able to allocate them to several plots and within the soil profile to the soil horizons. Furthermore, we modelled soil parameters that explained a certain variation of the amount of dissolved trace metals in a plot-specific way, depending on various biogeochemical soil parameters.

***Chapter 4***

Chapter four presents the results from the impact of successive anaerobic (simulated wet)-aerobic (simulated dry)-cycles in the laboratory on trace metal dissolution. Such laboratory experiments are important for simulating dynamic environmental conditions, carrying out specific settings in a shorter time frame than is possible in the field and also to be able to control a large number of variables. By carrying out those experiments we were able to control the redox potential and analyse several soil parameters under controlled conditions. We identified alluvial soils that are more pronounced to the simulated climate change scenario and increased amounts of dissolved trace metals than others. We could identify plot-specific trace metal release patterns during the experiment and thus we detected floodplain soils that might need special consideration under possible upcoming climate change adaptation measures. However, mainly due to temporal relations of biogeochemical processes in soils, several uncertainties remain making the interpretation of relating biogeochemical processes to trace metal release in those floodplain soils a very complex issue.

Chapter 2

# Trace metal dynamics in floodplain soils of the river Elbe: A Review

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*Journal of Environmental Quality 38:1349–1362 (2009)*

## Abstract

This paper reviews trace metal dynamics in floodplain soils using the Elbe floodplains in Germany as an example of extraordinary importance because of the pollution level of its sediments and soils. Trace metal dynamics are determined by processes of retention and release, which are influenced by a number of soil properties including pH-value, redox potential, organic matter, type and amount of clay minerals, iron-, manganese- and aluminium-oxides. Today floodplains act as important sinks for contaminants but under changing hydraulic and geochemical conditions they may also act as sources for pollutants. In floodplains such changes may be extremes in flooding or dry periods that particularly lead to altered redox potentials and that in turn influence the pH-value, the mineralization of organic matter as well as the charge of the pedogenic oxides. Such reactions may affect the bioavailability of trace metals in soils and it can be clearly seen that the bioavailability of metals is an important factor for estimating trace metal remobilisation in floodplain soils. However as bioavailability is not a constant factor, there is still a lack of quantification of metal mobilisation particularly on the basis of changing geochemical conditions. Moreover, mobile amounts of metals in the soil solution do not indicate to which extent remobilised metals will be transported to water bodies or plants and therefore potentially have toxicological effects. Consequently, floodplain areas still need to be taken into consideration when studying the role and behaviour of sediments and soils for transporting pollutants within river systems, particularly concerning the Water Framework Directive.

## 2.1 Introduction

For at least 200 yrs. the impacts of human activities on river systems have been noticeable. Since the beginning of industrialisation and an increase in population density, rivers have faced several water quality problems. Trace metal concentration in rivers increased markedly in Europe during the 19th and 20th centuries caused mainly by mining and industrial activities. Other important sources are sewage discharge, runoff, and atmospheric deposition. Since surface water concentrations of trace metals reached alarming proportions in the 1970s, regulations were implemented to control trace metal release at the source. But these implementations differ regionally; particularly in the river Elbe catchment intense and ongoing contamination lasted into the 1990s. However, even if harmful metal concentrations decreased in the river Elbe (tables of ARGE-Elbe, 1982–2005) and many western European rivers over recent decades, levels are still high compared to the original natural values (Mueller et al. 1994, European Environment Agency 1995, Negrel 1997, Soares et al. 1999, Qu and Kelderman 2001, Meybeck et al. 2007, Poot et al. 2007, Turner et al. 2008) and further target quality levels. According to the flood pulse concept (FPC, Junk et al. 1989), rivers and their fringing floodplains are integrated components of a single dynamic system, linked by strong interactions between hydrological and ecological processes. Tockner et al. (2000) expanded the FPC to more fully integrate temperate river-floodplain systems by adding the flow pulse to the flood pulse. Hence, it can be stated that for temperate river-floodplain systems the major driving force is the flow of the river that determines the degree of connectivity and the exchange processes of matter and organisms across river-floodplain gradients. As far as trace metals are concerned, riverine floodplains can adopt water quality functions for rivers during periods of flooding because flood events with river water are the main source for trace metal input into floodplain soils (Zerling et al. 2006). Consequently, the function of trace element storage results in a decrease of trace element load in the water body. As a result, river floodplains are usually heavily polluted and several studies have already described the high pollution due to trace metals of the floodplains of the river Rhine and Meuse (Middelkoop 2000, Hobbelen et al. 2004), Odra (Ciszewski et al. 2008) as well as the river Elbe (Duve 1999, Vogt et al. 2000, Schwartz 2001, Eisenmann 2002, Krueger and Groengroeft 2004) (Table 2.1).

*Table 2.1 Heavy metal and arsenic contents of the top soils of three main lowland rivers*

| | Elbe[1] | BV[2] | Rhine[3] [mg/kg] | BV[4] | Meuse[5] | BV[4] |
|---|---|---|---|---|---|---|
| As | 64 | 24 | 11.0 | | | |
| Cd | 4.4 | 0.3 | 1.41 | | 5.6 | 2.1 |
| Cr | 98 | 117 | 69.3 | | 328 | |
| Cu | 117 | 30 | 31.4 | 25 | 226 | 16 |
| Ni | 41 | 50 | 23.3 | | 81 | |
| Pb | 126 | 27 | 70.6 | 30 | 347 | 26 |
| Zn | 585 | 127 | 269 | 95 | 1593 | 82 |
| Hg | 5.6 | | | | | |

[1] *Summary of the contents of the top soils in the German part of the river (without tidal influence) mean values (Krueger and Groengroeft, 2004)*
[2] *BV= background values, summed by Krueger et al. (1999)*
[3] *Mean levels in top soils (0–10 cm), study area "Ewijkse Plaat" (Schipper et al. 2008)*
[4] *Summed by Thonon (2006)*
[5] *Average concentrations in top soils (0–10 cm) of hydric soils in the Biesbosch area (Rhine Meuse Delta) (Van den Berg 1998)*

Soil, with its potential to filter, buffer, and transform toxic substances, can be regarded as a key factor for environmental health and therefore, the knowledge of the retention and release of contaminants are among the most important chemical processes to be understood in soils (Graf et al. 2007). Since retention and release are influenced by several soil properties including pH-value, redox potential, organic matter, type and amount of clay minerals, iron, manganese, and aluminium-oxides, contaminated sediments are also considered to be a large eco-toxicological risk to the aquatic environment (Burton 1992, Brack et al. 2007) because they may act as not only important sinks but also as sources of contaminants (Calmano et al. 1993, Schwartz et al. 2006) under changing hydraulic and geochemical conditions (Van der Veen et al. 2006).

The relative mobility of trace elements in soils is of major importance with regard to their plant availability and their potential for leaching down soil profiles to the groundwater (Alloway 1997). Thus the bioavailable fraction may be a better indicator to assess the risk of metal polluted sediments and floodplain soils (Peijnenburg and Jager 2003, O'Halloran 2006). This review deals with soil properties affecting the processes of retention and remobilisation including bioavailability of metals in soils but in particular in floodplain soils along the river Elbe in Germany. For this purpose scientific papers and book chapters concerning trace metal mobility in soils, in floodplain soils as well as in the Elbe floodplains have been reviewed. The importance of the Elbe floodplain data are reflected by the shear size of the river Elbe (Fig. 2.1) which counts as one of the largest rivers in Central Europe and moreover one of the most polluted rivers in Europe by the end of the 1980s (Adams et al. 1996).

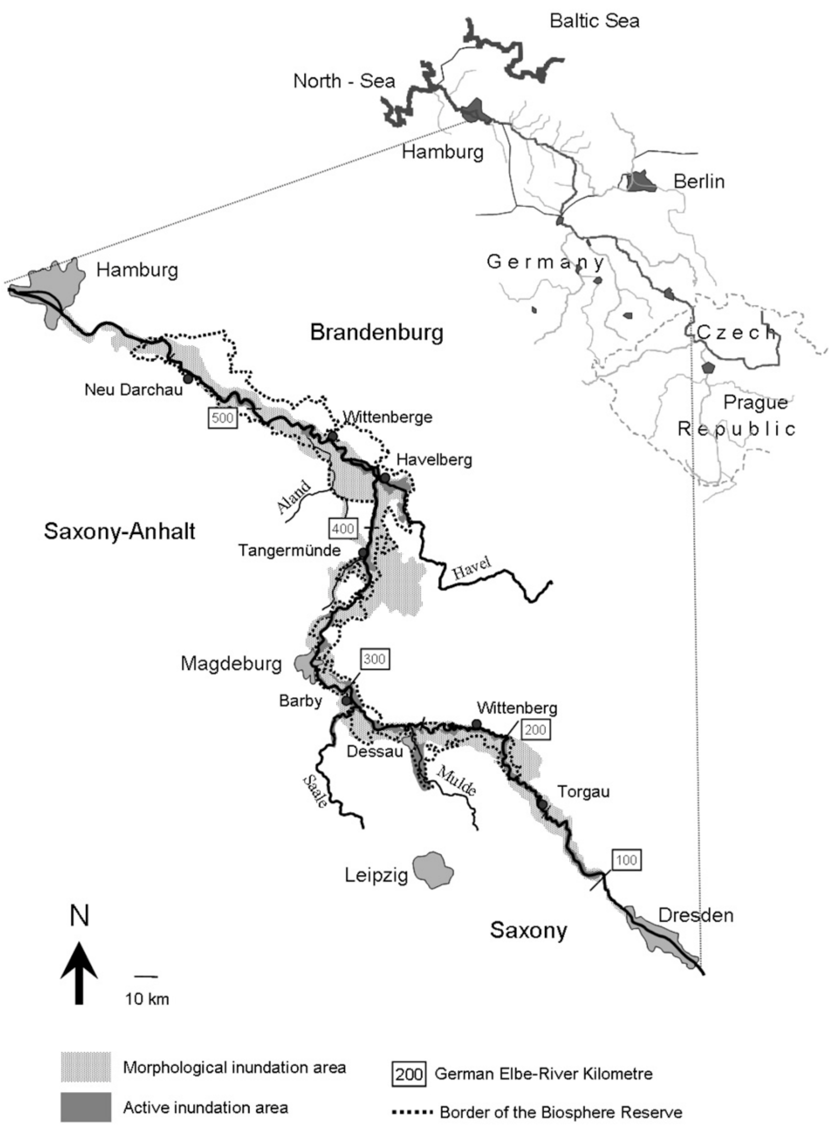


Figure 2.1 The river Elbe in Germany (Scholten et al. 2005)

Numerous chemical plants are located along its banks as well as along the tributaries of the upper Elbe course in the Czech Republic. Furthermore, a number of chemical plants and large industrial areas are situated along its middle course. The lower course of the river Elbe runs through the city of Hamburg, receiving a significant load of contaminants originating from municipal and industrial sewage. Main tributaries of the river Elbe like the river Mulde still have high loads of trace metals and substantially contribute to the load of the river Elbe (Klemm et al. 2005). Even when the contamination input was reduced as a result of technical improvements, sediment toxicities remained at a high level (Duft et al. 2003). Sediments constitute the "long- term memory" of river water quality and pollutant discharge over decades results in highly polluted sediment (Zerling et al. 2006). Sediment from the Elbe riverbed and subsequently the Elbe floodplains show considerable contamination by trace metals, where the highest contamination can be found in low lying areas like depressions (Krueger et al. 2005, Rinklebe et al. 2007). The enrichment factor in sediments during a recorded period toward the geogenic background varies between 8 (arsenic) and 100 (mercury, median values, n=23) (Krueger et al. 1999). In 85% of the investigated sites from a study performed by Groengroeft et al. (2005) topsoil contamination of mercury is above the action value (2 mg/kg) of the German Soil Protection Guideline (BBodSchV 1999). Though precise input/output calculations are missing, it can be estimated that Elbe floodplains act as net sinks for contaminants so far (Schwartz 2001). The extreme summer flood in August 2002 (Engel 2004) showed that polluted alluvial soils in the catchment can also act as sources for trace metals under certain circumstances. Flood events of this extent show an enormous additional mobilisation potential (BfG 2002). Sources for pollution input, which are higher than the common amount, are, among others, inundation areas, since most of the pollutants are bonded with sediments (BfG 2002). Distinct increases in particulate bounded arsenic (3.6–10.8 times) and lead levels (1.4–4.5 times) were found at the beginning of the flood (Tab. 2.2) (BfG 2002). These concentrations decreased by approximately 50% in the further course of the flood, but even after the flood, elevated concentrations were still found in the suspended solids in the river water. Other trace metals (cadmium, copper, nickel) were only elevated at the beginning of the flood and in turn others were subject to a significant dilution (mercury, zinc) (BfG 2002).

*Table 2.2* *Pollution of suspended solids of the river Elbe near Magdeburg with heavy metals (mg/kg), comparison between the flood event in August 2002 and the average content during standard discharge conditions (BfG 2002)*

| | As | Pb | Cd | Cr | Cu | Ni | Hg | Zn |
|---|---|---|---|---|---|---|---|---|
| Mean *(n=7, flood event August 2002) suspended solids Elbe near Magdeburg* | 160 | 307 | 6.3 | 114 | 126 | 61 | 2.2 | 880 |
| Mean *(Year 2000, standard value) suspended solids Elbe near Magdeburg* | 30 | 122 | 6.7 | 112 | 117 | 57 | 4.9 | 125 |

## 2.2 Soil properties and trace metal dynamics

Trace elements are normally present at relatively low concentrations in soils or plants whereby some are essential for plants, animals, or humans (Pierzynski 1994). Soil is the ultimate and most important sink of trace elements in the terrestrial environment, but approaching or exceeding the soil binding capacity may lead to several environmental consequences, including increased mobility in the soil system (Adriano 1986). The soil solution is the medium in which all soil reactions occur and the pore-water concentrations are considered to be the most sensitive parameters of environmental change (Adams 1994). Thus information on soil solution composition is crucial for understanding the chemical processes that control, among others, bioavailability and mobility of elements (Harter and Naidu 2001, Calmano et al. 2005). Soil solution composition varies significantly depending on soil type and the soil environment, like for example seasonal fluctuations in temperature, deposition rates, and biomass production (Song and Mueller 1995). In wetlands, the concentration of trace metal ions removed from solution is determined by interacting processes of sedimentation, adsorption, co-precipitation, cation exchange, complexation, microbial activity, and plant uptake (Matagi et al. 1998). The extent to which these reactions occur and consequently how metal activity in the soil solution is controlled is generally considered to be the result of metal equilibrium between clay minerals, organic matter, and hydrous oxides, with the soil pH-value and redox status strongly affecting these equilibriums (Lindsay 1979, Matagi et al. 1998, Van Griethuysen et al. 2005). Plants also have the capacity to accumulate trace elements, although this is also limited. Consequently, trace metal overloads can lead to phytotoxicity (Adriano 1986). The content of metals absorbed by plants from the soil solution is mainly dependent on the total amount of ions in the soil solution as well as on the amount and surface of the root network (Alloway 1997). Because the processes are dependent on each other, it is difficult to illustrate what actually occurs or which reactions take place, thus making the whole process of metal removal mechanisms in wetlands very complex (Matagi et al. 1998) (Fig. 2.2).

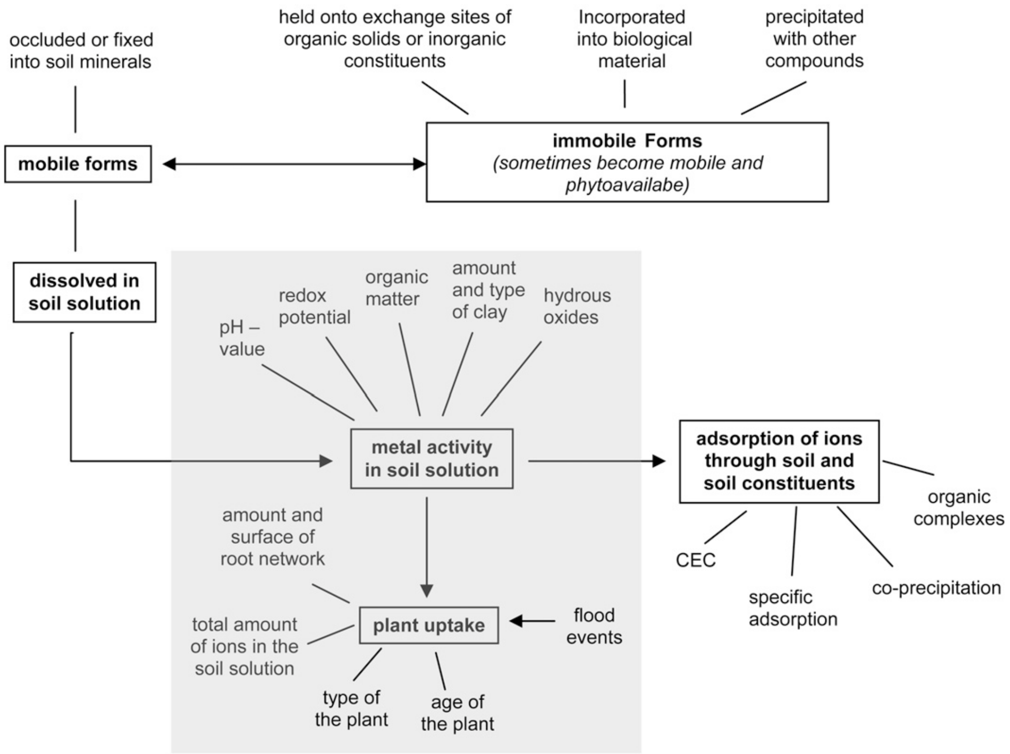


Figure 2.2 Overview of processes and factors that affect trace metal mobility
*(gray box indicates factors covered in the review)*

## 2.3 Key characteristics of soils including floodplain soils

### 2.3.1 Redox potential

In floodplain soils, which are characterised by fluctuating water tables with the effect of water saturation and inundation for parts of the year, the oxidation–reduction cycle plays an important role in the soil system. Particularly microbial and also chemical processes are affected by changing water contents. Floodplain soils are characterised by both: dry conditions, similar to upland soils (Gambrell 1994) and wet conditions, similar to waterlogged/wet soils. Soil chemical and microbial processes affect, among others, trace metal mobility and the bioavailability in wetland soils (Gambrell and Patrick 1988, Gambrell et al. 1991a, 1991b). The behaviour of trace elements in sediments is to a large extent controlled by the redox cycles of the major biogeochemical elements (Shaw et al. 1990). Furthermore, Hamilton-Taylor and Davison (1995) conclude that the mobilisation of trace metals in sediments is strongly dependent on redox gradients. The redox status in wetland soils is strongly dependent on seasonal fluctuations like temperature, and the hydrological regime as well as the availability of organic matter (Olivie-Lauquet et al. 2001). Additionally, trace element release occurs in phases with a decline of the redox potential of the soil solution and coincides with an increase of temperature and dissolved organic carbon content of the soil solution (Olivie-Lauquet et al. 2001). This is because higher temperatures favour microbial activity in sediment and dissolved trace metal concentrations significantly increase by complexation with organic ligands in the pore water (Van den Berg et al. 2000). Hence seasonal changes in the redox state lead to seasonal changes in trace metal mobilisation (Shiller 1997). Olivie-Lauquet et al. (2001) strongly suggest that the soil microbial population may play a dominant role in controlling the seasonal release of trace elements into the soil solution through catalysing sesquioxides as electron acceptors induce changes in the redox potential and the increase in dissolved organic carbon content. Furthermore, in floodplain soils the respective duration of the reduced or oxidised phase plays an essential role in the formation of various crystalline oxides and in the remobilisation of co-precipitated and specifically adsorbed trace metals. Schwartz (2001) describes altered redox bonds through multiple high-water phases of the Middle Elbe River and documents the cumulative dissolution of iron links during reduced conditions.  It is to be noted thereby that not every flood leads to a lowering of the redox potential. In the context of field studies Schwartz et al. (1998) also prove that the course of the redox potential is dependent on the quantity of organic substances and temperature. They come to the conclusion that even smaller amounts of water in the soil are sufficient to bring about a reduction in the redox potential if the organic matter content and the temperature are favourable. On the other hand, low soil temperatures with high water content also result in the redox potential remaining in a positive range (Fig. 2.3).

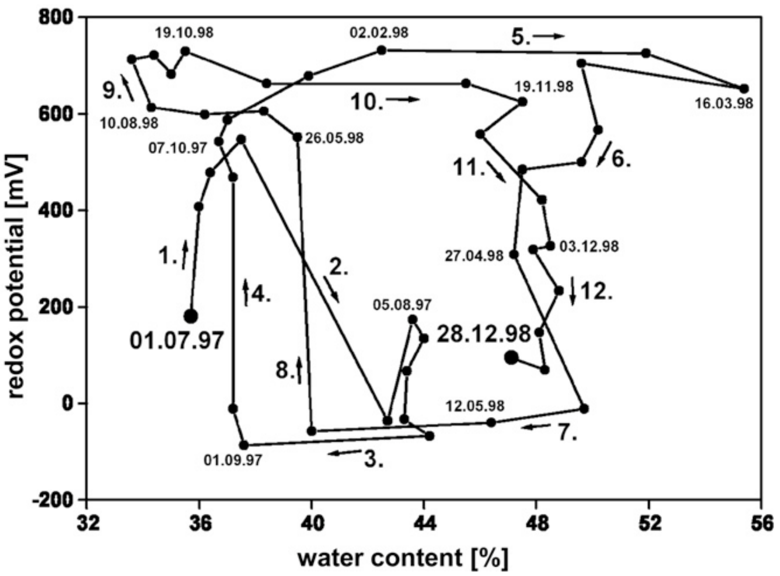


Figure 2.3 Relation between water content and redox potential during changing soil temperatures within a cohesive, organic matter rich horizon during a period of 18 month (Schwartz 2001)

From this Schwartz et al. (1998) conclude that summer season flood waters have a more pronounced effect on chemical mobilisation of matter than winter season flood waters. In contrast however, the fluctuation range of the redox potential is highest in soils of flow cut depressions and flood channels which are rich in humus, as confirmed by Schwartz et al. (1998)

in their comparison of a plateau and depression location. Moreover, in laboratory experiments the redox sensitivity of Middle Elbe floodplain top soils is ascertained by Heinrich et al. (2000). They showed that the duration of the high-water phase influences the behaviour of redox potentials. Particularly in top soils, significant alterations in the redox potential were determined, which can be attributed to the presence of decomposable carbon content. With regard to proper metals, contrary results regarding the influence of the redox status on trace metal mobility were found in laboratory investigations. For lead, zinc, and cadmium, increased mobility relates with decreasing redox potentials were determined (Ng and Bloomfield 1962, Chuan et al. 1996). In contrast, some author's report that low $E_H$ values does not favour an increase in metal solubility. For cadmium, a decrease in bioavailability in waterlogged soils due to the formation of cadmium sulfide is described by (Xiong and Lu 1993, Alloway 1997). In laboratory studies Gambrell et al. (1980) also describe decreasing water soluble zinc contents with decreasing $E_H$ values. In addition, Sims and Patrick (1978) found in their laboratory studies decreasing zinc concentrations at low $E_H$ values. In field studies along the Middle Elbe River Schwartz et al. (2004) found increasing zinc concentration following the reduced phase in which zinc was fixed as sulfide. Due to oxidation and mobilisation zinc migrated into the soil solution.

### 2.3.2 Organic matter

Degradation of organic matter is the main biogeochemical process taking place in recently deposited sediments (Berner 1980). With regard to the different chemical conditions in soils, different redox reactions dominate the decomposition of organic matter. Freshwater sediments with generally high organic matter content show rapid consumption rates of organic matter (Calmano et al. 2005). Furthermore, the decomposition of organic matter is stimulated by alternately wetting and drying the soil (Reddy and Patrick 1975). During the early diagenesis of sediments, the mineralisation of organic matter, which is mainly biologically catalysed, is one of the important reactions determining the fate of trace metals in sediments (Calmano et al. 2005). Furthermore, other scientist's state that the organic substance of soils represents a significant impact on the retention of trace metals on both the formation of organic- metallic complexes and adsorption (Blume and Bruemmer 1991, Alloway 1997, Rieuwerts et al. 1998, Kabata-Pendias 2001, Olivie-Lauquet et al. 2001). Dissolved organic carbon, in particular, primarily influence the formation of soluble metal-organic complexes (Olivie-Lauquet et al. 2001, Scheffer and Schachtschabel 2002). Consequently, Olivie-Lauquet et al. (2001) describe the content of dissolved organic carbon as the possible key factor determining whether wetlands behave as either sinks or sources for substances. Van Griethuysen et al. (2005) also summarise that organic carbon degradation and resulting redox processes play a key role in the mobility of sediment-bound contaminants.

On the basis of empirical correlations Krueger et al. (2005) state the importance of soil carbon as an indicator for soil contamination in the Elbe floodplains. The correlation result from the high amounts of organic matter in the sediments acting as the dominant binding phase for trace metals. Furthermore, Krueger et al. (2005) determined a relation between elevation and flooding frequency to the content of total organic carbon in floodplain soils. Hence, they were able to prove higher quantities of organic carbon and, consequently, higher quantities of bonded trace metals in lower situated geomorphological structures like depressions of the Elbe floodplains. Eisenmann (2002) also investigated high carbon contents along the Middle Elbe and analysed linear correlations between organic matter and trace metals, where closer correlations were found in the study site of the floodplain (Fig. 2.4). Here coherences between industrialisation and increased anthropogenic carbon were obvious (Schwartz 2001). For the River Meuse floodplains Albering et al. (1999) also determine significant correlations between the organic matter fraction and the trace metal content in the soil. Similar results were also found by Van den Berg et al. (2000) in laboratory studies. They interpret the correlation between metal and organic matter not in the way that organic matter is the active adsorptive phase for trace metals. Instead, they discuss that the correlation is because of the presence of organic matter and oxides in the finest fraction as well as the formation of organic and oxide coatings on clay minerals.

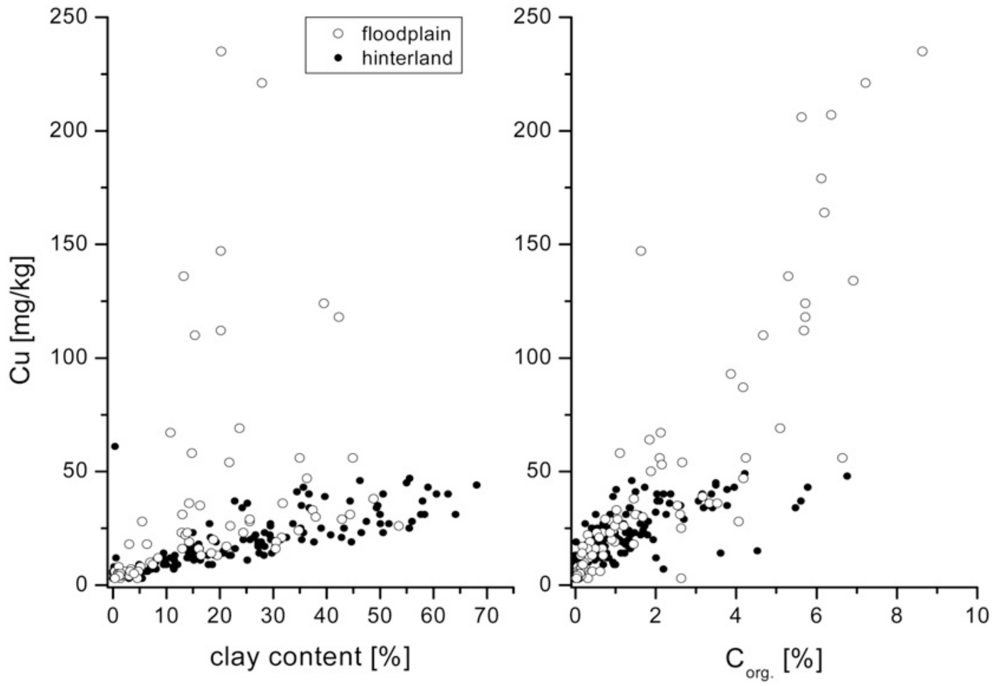


Figure 2.4 Total copper content in floodplain soils in relation to clay content and organic carbon (Eisenmann 2002)

For a depth profile within the Mulde River floodplain, a tributary of the river Elbe, Krueger and Neumeister (1999) proves that copper and lead (70% respectively) are bonded, primarily organically as well as on badly crystallized iron-oxides, nickel is located in an easily ascertainable fraction and cadmium in the mobile fraction. Also within the Mulde floodplain, but through experiments with small monoliths, Kalbitz and Knappe (1997) surmise that the impacts of the soil organic matter on the mobility of trace metals is dependent of the respective metal and is then particularly significant when stable complexes are formed with organic matter. They went on to show that the effects of the organic matter on trace metal mobilisation essentially depend on the location and the resulting differences in the composition of the soil solution and the quantity and quality of the organic matter. However, the soil organic matter is of lesser significance with pH values lower than 4.5 (Kalbitz and Wennrich 1998).

### 2.3.3 pH-value

Most trace metals become more mobile in increasingly acid conditions (Alloway 1997). Therefore, the pH-value is generally acknowledged to be the principal factor governing concentrations of soluble and plant available metals (Brallier et al. 1996). The importance of the pH-value however is not only given by itself but also by the fact that the pH-value affects other important factors on metal solubility (Harter and Naidu 2001). It influences the surface load of silicate clays, organic substances, and both iron and aluminium-oxides. Furthermore, the pH-value affects precipitation and solution reactions, the redox potential, mobility and distribution of colloidal matter as well as the bioavailability of metal ions. Additionally, the pH-value exerts influence on the sorption of cations and on the formation of organic-metallic complexes (Adriano 2001). Herms and Bruemmer (1984) determined in laboratory studies that the influence of soil reaction on the solubility of trace metals decreases as follows: Cd > Ni > Co > Zn > Cu > Pb > Hg. This sequence clarifies, according to Harres (1998) the fact that one has to expect a higher mobile proportion of easily dissolved metals in acidified soils than in neutral soils, even if the total content of trace metals is low. In laboratory studies Gambrell et al. (1980) investigated pH-values in a floodplain of silt loam soil under changing redox conditions; pH-values under continuous flooding range from 6.9 to 7, under intermediate oxidation from 5.8 to 6.2, under oxidised conditions from 5.1 to 6.2 and came to the result that the pH-value can change greatly as a consequence of flooding-drying cycles. The significance of the pH-value for trace metal mobilisation in floodplains of the river Elbe could be proved through field data (Schwartz 2001, Eisenmann 2002, Krueger and Groengroeft 2004). So far unpublished data from the Ad Hoc project 2002–2004 shows a range of measured pH-values ($CaCl_2$) between 4 and 6.9 (median 5.8). These values reflect the investigation of higher elevated (lower pH-values) and lower elevated (higher pH-values) sites along the river Elbe. In this range for cadmium, nickel, zinc, and even for mercury a relatively high mobility can be expected, whereas arsenic and chromium are only moderately mobile and copper and lead are relatively immobile (Adriano 1986).

Krueger et al. (2004b) presented a mobility row for river Elbe alluvial soils, which show the percentage of the mobile amount compared to the total amount Cd(3.6%) >> Zn(0.9%) > Cu(0.2%) >> As(0.07%) > Pb(0.03%) (n=16) under field conditions. It corresponds with the row of binding strength from Herms and Bruemmer (1984) and also reflects the classification from Adriano (1986). Furthermore, other scientists examined the highest mobile and thus eco-toxicological relevant amounts of cadmium and zinc in alluvial soils (Hoehn et al. 2000, Oka/Elbe project 1996–1999, unpublished; Schwartz 2001), which is due to the higher limit pH-values. Eisenmann (2002) confirm the high significance of the pH-value for the bioavailability of cadmium in floodplain soils of the Middle Elbe River. Above the limit pH-value of cadmium (pH-value = 6) 1.7 to 6.0% of the total cadmium content are found in the mobile phase. In medium acidic soils (pH-value = 5–6) 30 to 50% of the total cadmium content are mobilised in the soil solution (Eisenmann 2002) (Table 2.3). In this context the importance of the organic matter as sorbent is obvious. At a pH level of 5.4 and a carbon content of 4.2% more than 50% of the total cadmium content are available whereas with increasing carbon content (5.6%) just 41% of the total cadmium is available (Eisenmann 2002). Investigations carried out by Geller et al. (2004) show for 77 of 114 sampling sites along the German river Elbe and its tributaries pH-values that are lower than 6. Therefore at about 67% of the study sites up to 50% mobile amounts of cadmium may be expected. Indeed, it is well known that its availability increases considerably even with minimal acidification, but the presence of sulfate and chloride ions exerts an additional degree of increase in solubility, since they form, together with cadmium, soluble inorganic complexes.

*Table 2.3 Mobile amounts of cadmium in studied floodplain soils dependent on pH-value (Eisenmann 2002)*

| sample | pH value ($CaCl_2$) | $Cd_{total}$ (AAS, aqua regia dissolution) | $Cd_{dissolved}$ ($NH_4NO_3$)[1] | Mobile amount (%) |
|---|---|---|---|---|
| Vega-Gley a) | 5.7 | 5.4 | 1.82 | 34 |
| Vega-Gley b) | 5.4 | 10.2 | 4.24 | 41 |
| Vega | 6.4 | 11.3 | 0.69 | 6 |
| Gley-Vega | 7.1 | 10.4 | 0.31 | 3 |
| Gley-Regosol a) | 7.4 | 10.2 | 0.17 | 2 |
| Gley-Regosol b) | 7.1 | 1.9 | 0.04 | 2 |
| Norm-Vega | 5.4 | 1.7 | 0.87 | 51 |

[1] *According to Zeien and Bruemmer (1989)*

### 2.3.4 Hydrous oxides

Hydrous oxides of iron, manganese, and aluminium are known as an important soil component controlling the retention of trace metals in soils (Jenne 1968, Bruemmer et al. 1986, Gambrell 1994, Rate et al. 2000, Trivedi and Axe 2000, Dong et al. 2005). However, hydrous oxides also contribute to a dynamic trace metal fraction in soils, because in an oxidising, dry environment, they evolve to more crystalline and stable structures, which can immobilise trace metals (Alloway 1997, Tack et al. 2006). Alternatively, if soils are reduced, trace metals can be released into the soil solution by the reductive dissolution of manganese and iron-oxyhydroxides (Davranche and Bollinger 2000a, Grybos et al. 2007). As a result, Grybos et al. (2007) summarise the importance of manganese and iron-oxyhydroxides as major parameters controlling trace metal mobility in wetland soils. However, the remobilisation process always depends on the redox condition as well as on the single element. For example, metals fixed through adsorption cadmium stays in the solution after remobilisation whereas lead may be re-adsorbed very fast. However for metals fixed in the co-precipitation process (metals substituted in the solid matrix) the risk of contamination is greater for lead than for cadmium (Davranche and Bollinger 2000b). Hence, metal ions show different adsorption affinities to oxides: Pb>Cu>Zn>Cd>Co>Mn>Sr>Ca (Trivedi and Axe, 2000) and among the oxides various bonding preferences exist in reference to trace metals: manganese-oxides mainly adsorb copper, nickel, cobalt and lead, and iron- and aluminium-oxides mainly lead and copper (Adriano 2001). Manganese oxides have higher binding capacities than iron oxides (Kuntze and Herms 1986), but since iron-oxides are quantitatively dominant in soils, these play the most important role in binding trace metals (Harres 1998) whereas Kabata-Pendias (2001) consider both iron and manganese-oxides to be among the most important pedogenic oxides in binding trace metals. In soils, iron occurs in different associations, which show different affinities in binding trace metals: ferrihydrite>goethite>haematite (Kuntze and Herms 1986). The mineralogy of manganese is much more complex; large amounts of oxides and hydrous oxides in which substitutes of $Mn^{2+}$, $Mn^{3+}$, and $Mn^{4+}$ occur are widespread (Fittschen and Groengroeft 2000). In hydromorphic soils in particular, amorphous ferrihydrite dominates the soils (Kuntze and Herms 1986). This is proven by Fittschen and Groengroeft (2000) for investigated soils along the Middle Elbe. They describe a high activity level ($Fe_o/Fe_d$)[2], which describes the easy mobilisable amount of iron among the iron oxides. That concludes that the iron-oxides examined mainly consist of ferrihydrite within the zone where groundwater fluctuates. Crystalline oxides like goethite are subordinately significant. Contrary to Bruemmer et al. (1986) and Blume and Bruemmer (1991) correlations between total iron and clay content is much less significant in floodplain soils because of the translocation of iron ions through hydromorphic processes, whereas the total content of manganese also in terrestrial soils are almost not dependent on the clay fraction (Eisenmann 2002). For arsenic also Schwartz (2001) has examined that it is primarily bonded by hydrous oxides in soils of the Middle Elbe that goes along with the findings of Eisenmann (unpublished) (Fig. 2.5); under oxidised conditions arsenates exist, while under reduced conditions arsenites occur. Maximum contents of arsenic

[2] $Fe_o$=oxalate soluble iron, $Fe_d$=dithionite soluble iron

could be found in the floodplain in an iron-oxide rich sub-soil horizon and furthermore a clear relationship between the content of oxalate-dissolvable iron and arsenic was examined (Schwartz, 2001). Therefore Schwartz (2001) comes to the conclusion that a parallel precipitation of arsenic ensues with the formation of iron-oxides.

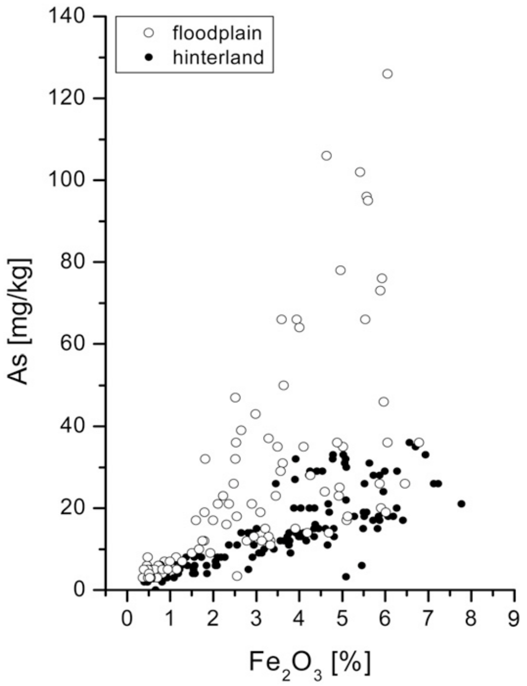


Figure 2.5 Total arsenic content in floodplain soils in relation to iron (III) oxide (Eisenmann unpublished) *(Data collected during the project: „Rückgewinnung von Retentionsflächen und Altauenreaktivierung an der Mittleren Elbe in Sachsen-Anhalt (FKZ: 0339576)")*

### 2.3.5 Clay content

Even if clay minerals have only a low influence on metal retention in comparison to iron and manganese oxides as well as to organic substances, they have a significant importance because of their large quantity in soils (Kuntze and Herms 1986, Blume and Bruemmer 1991, Kabata-Pendias 2001). More important than the content however is the type of clay minerals that occur in soils (Kuntze and Herms 1986, Rieuwerts et al. 1998). According to Kuntze et al. (1984) the exchange capacity of clay minerals in- creases as follows: kaolinite < chlorite < illite < montmorrillonite < vermiculite. Additionally the sorption capability of clay substances is considerably dependent on the pH-value; but even in highly acidic pH-ranges high clay contents lead to declined metal solubility (Kuntze and Herms 1986). Furthermore, soils with higher clay contents have higher values for cation exchange capacities, which made more unspecific adsorption space available under acidic conditions in soils that lead to higher adsorption rates and therefore to reduced solubility of trace metal in soils (Herms and Bruemmer 1984). In this respect, Harres (1998) concluded that, for soils in which other sorption-capable groups of matter are minimally represented, clay can play the most important role in the sorption of metals. In the soils of the Middle Elbe River, illites were identified as the dominant clay mineral, followed by kaolinites and, closely, by certain mixed-layer minerals (Oka/Elbe project 1996–1999, unpublished). That leads to the assumption that the soils of the Middle Elbe River, concerning clay content as a sorption agent, have a medium capacity for metal exchange. Hence, Eisenmann (2002) determined a linear dependence of clay content and anthropogenically unaffected trace metal contents for soils along the Middle Elbe (Fig. 2.4). With 116 analytical experiments involving the coarseness of top soils between stream km 128 and 493 it is proven that silt-dominated, fine-grain soils characterise the floodplain loam cover along the Elbe (Ad Hoc project, 2002–2004, unpublished data). Differences in the make-up of the granular sizes can also be ascertained for different morphological units of the floodplain along the Lower Middle Elbe. For example, a clear dominance of clays and silts can be determined (approximately 90%) at depression locations. On the other hand, sand makes up around 45% of the soil substrata at plateau locations. This agrees with the investigations of Krueger et al. (2005), Poot et al. (2007), and Rinklebe et al. (2007) that higher trace metal contents are found in lower situated geomorphological forms like depressions and lower ones in higher situated forms like plateaus. Furthermore, Krueger et al. (2004b) found correlations between the content of organic matter and clay content; finer grained soils show higher contents of organic matter (Krueger et al. 2005). In contrast, Albering et al. (1999) also do not observe any relationship between the trace metal content in soils and the clay fraction (<2µm) for the River Meuse.

### 2.3.6 Plant uptake

Plant availability of certain metals depends on soil properties such as pH-value, redox conditions, metal concentration in the soil solution, cation exchange capacity, soil aeration, clay content, organic matter content, and fertilization as well as on factors specific for plants like competition between plant species, the type of plant, it's size, the root system, and the stage of the development of the plant (Sims 1986, Fergusson 1990, Davies 1992, Albering et al. 1999, Kabata-Pendias 2001, Krueger and Groengroeft 2004, Groengroeft et al. 2005, Overesch et al. 2007). Climatic conditions also influence the rate of trace metal uptake; a higher ambient temperature leads to a greater uptake of trace elements by plants (Kabata-Pendias 2001). The distribution of metals among several soil fractions also plays an important role (Xian and Shokohifard 1989). According to Tessier et al. (1979) metals can be found in five fractions: (i) exchangeable, (ii) associated with carbonates, (iii) associated with oxides, (iv) associated with organic matter and/or sulfides, and (v) residual. Trace metals in exchangeable forms have the highest solubility, thus giving the highest potential bioavailability relative to other fractions (Xian and Shokohifard 1989). However, when the soil pH-value is low enough, carbonate-associated metals are also easily released into the solution (Barona and Romero 1997) and also root exudates can solubilize metals (Youssef and Chino 1991).

There are three general uptake characteristics: accumulation, indication, and exclusion, which mainly depend on the specific ability of plants and huge differences in metal uptake between plant species (Kabata-Pendias 2001). The main source for trace metals in plants is their growth media, from which the absorption by roots is the main pathway of trace elements to plants (Fergusson 1990, Kabata-Pendias 2001). However, in flooded areas the particular enrichment on plant surfaces has to be additionally taken into account (Krueger and Groengroeft 2004, Groengroeft et al. 2005). After the extreme Elbe flood in 2002 Groengroeft et al. (2005) found vegetation contaminations through deposited sediments on plant surfaces that preclude grazing. The contamination level had already gone down considerably after 1 month, but still half of the samples indicated threshold values of the EU-directive on undesirable substances in animal feed (Groengroeft et al. 2005). However, the ability of different plants to adsorb metals varies greatly and further elements show different susceptibility to phytoavailability than others. Kabata-Pendias (2001) describe for example cadmium are taken up very easily, while zinc, mercury, copper, lead, and arsenic are only averagely taken up and nickel and chromium only slightly available to plants. Krueger and Groengroeft (2004) gives an overview about several metal concentrations in the top soils of the river Elbe floodplains compared to action values for grasslands of the German Soil Protection Guideline (Table 2.4) (BBodSchV 1999). The study shows that the exceedances vary between metals. One-half of the samples show transgressions concerning arsenic, whereas only three samples show it for cadmium. About 70% of the samples are highly contaminated with mercury (above the threshold value) and approximately 25% with copper. In spite of these contaminations, it is always difficult to find intercorrelations between soil and metal uptake by plants in floodplains (Krueger and Groengroeft 2004, Groengroeft et al. 2005).

*Table 2.4* *Percentiles of heavy metal and arsenic contents of German river Elbe alluvial top soils (Krueger and Groengroeft 2004), exceedance of action values in bold*

| | As | Cd | Cr | Cu<br>*mg/kg* | Hg | Ni | Pb | Zn |
|---|---|---|---|---|---|---|---|---|
| Minimum | 3 | 0.1 | 10 | 8.8 | 0.2 | 7 | 11 | 34 |
| 10% | 20 | 0.8 | 32 | 26 | 1 | 18 | 42 | 135 |
| 20% | 31 | 1.6 | 52 | 54 | 1.7 | 27 | 74 | 264 |
| Median | 50 | 3.1 | 82 | 96 | 3.5 | 38 | 110 | 482 |
| Mean | 64 | 4.4 | 98 | 117 | 5.6 | 41 | 126 | 585 |
| 75% | 91 | 5.7 | 126 | 156 | 8 | 48 | 160 | 749 |
| 90% | 130 | 9.4 | 185 | 252 | 13 | 65 | 224 | 1273 |
| Maximum | 200 | 30 | 355 | 540 | 31 | 140 | 370 | 2500 |
| Action value for grassland [1] | 50 | 20 | - | 1300<br>*(200 for sheep grasing)* | 2 | 1900 | 1200 | - |

*[1] according to 8 par. 1 set 2 nb. 2 of the German Soil Protection Guideline concerning the transfer of pollutants from soil to crop plants in grasslands regarding the quality of plants (mg/kg dry weight, grain size < 2 mm, arsenic and trace metals in aqua regia dissolution, analytics according to appendix 1) (BBodSch, 1999).*

This is because metal concentrations in plants vary not only according to metal mobility in floodplain soils but also depending on element, plant species, the sampled plant organ and the sampling date (Krueger and Groengroeft 2004, Groengroeft et al. 2005, Overesch et al. 2007). In this respect Krueger and Groengroeft (2004) found non-significant relationships between soil and grassland plant loads for arsenic, mercury and lead (Fig. 2.6). Metal enrichments were found in plants on soils with high and low pollution. In contrast, for cadmium they found weak correlations between metal content in soil and plants, even if cadmium showed only a smaller total content in the soil samples. The enrichment of cadmium in plants growing on river Elbe alluvial soils with pH values lower than 6 cannot be excluded, although soil action values of 20 mg/kg are met (Krueger and Groengroeft 2004, Groengroeft et al. 2005). This is confirmed by Groengroeft et al., 2005 who even found significant positive correlations between the mobile soil fractions and the plant contents for cadmium ($P<0.001$). However, they go even further and present a row for plant availability of several metals based on data from Elbe floodplain top soils (Fluvisols and Cambisols) ($NH_4NO_3$ extracted): Cd > Zn > Cu ≈ Pb > As > Hg, which is confirmed by Overesch et al. (2007) who not only investigated Fluvisols, but also Regosol and Gleysols along the river Elbe ($NH_4NO_3$ extracted): Cd > Zn > Ni > > Pb, Cu > As, Cr, Hg. For the River Meuse Albering et al. (1999) show similar results. Trace metal concentrations in crops grown on enriched floodplain soils are within the range of concentrations found in crops grown on un-contaminated soils. The exception is cadmium, which was enriched in wheat *(Triticum aestivum L.)* in relation to relatively low levels in soil, but under pH values that ranged from 5.5 to 7.3. Overesch et al. (2007) take this further and state metal content for individual plant species on regularly flooded soils that are used as extensive grassland. By far the highest concentrations [mg/kg] of cadmium (4.62), copper (34.6), and mercury (0.13) are measured in Artemisia *(Artemisia vulgaris L.)*. Maximum values of arsenic (2.63) are found in alopecurus *(Alopecurus pratensis L.),* whereas phalaris *(Phalaris arundinacea L.)* shows maximum values of nickel (18.6), lead (4.15), and zinc (199.0).

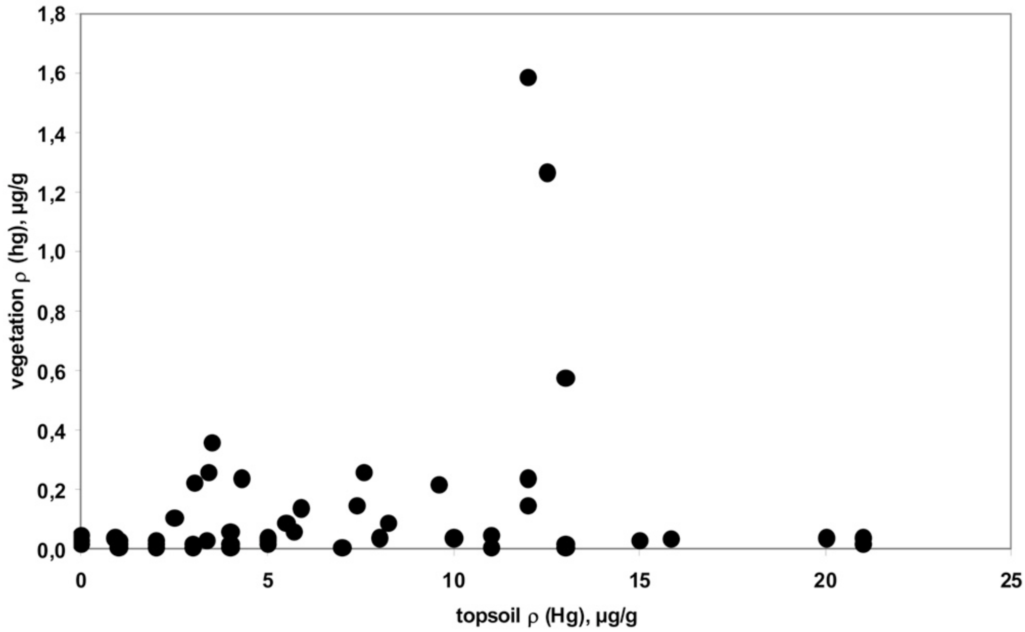


Figure 2.6: Mercury contents in river Elbe alluvial top soils and plants (Krueger and Groengroeft 2004)

## 2.4 Concluding remarks and further research

River floodplains are characterised by a high degree of variability in the frequency and the period of inundation of the various morphological forms (Baldwin and Mitchell 2000). Spatial variations in metal concentrations in overbank sediment deposited during a flood are controlled by differences in clay and organic matter contents in the sediment (Middelkoop 2000). The largest amounts of metals accumulate near to the natural levee, and in low-lying areas that are frequently inundated and where large amounts of fine sediments are deposited (Middelkoop 2000, Krueger et al. 2005). In this respect floodplains show a high variability of diffuse soil contamination where low pollutant concentrations can be found only a short distance from sites with high contamination (Kooistra et al. 2001). Even if water quality in European lowland rivers has improved over recent decades, sediments reaching river floodplains through inundation events still transgress threshold values for several metals (Albering et al. 1999, Krueger and Groengroeft 2004). Thus, sediments along European lowland rivers still show high levels of contamination due to the long period of contamination (Van der Veen et al. 2006). Organic matter, clay minerals, and hydrous oxides behave, so far, as sinks for trace metals in floodplain soils. But since processes and factors and the metals itself strongly influence each other correlations are not always obvious especially when considering field data. For example, Table 2.5 shows that mercury strongly correlates with organic carbon (0.37) but is still not significant (P=0.12).

*Table 2.5 Correlation matrix of analysed parameters for 18 samples of Elbe floodplain top soils (unpublished data of Leuphana University surveyed during the EU-Project RAMWAS between 2007 and 2008).*

| | Clay | Silt | Sand | Finest Fraction | $C_{org}$ | Hg |
|---|---|---|---|---|---|---|
| Clay | 1 | | | | | |
| Silt | -0.81 | 1 | | | | |
| Sand | -0.30 | -0.31 | 1 | | | |
| Finest Fraction | 0.83 | -0.41 | -0.68 | 1 | | |
| $C_{org}$ | 0.20 | -0.12 | -0.14 | 0.06 | 1 | |
| Hg | 0.05 | -0.02 | -0.06 | -0.00 | 0.37 | 1 |

However, since the effects of climate change described it may lead to changes in physico-chemical conditions, which control the availability of trace elements in sediments (Poot et al. 2007). Thus trace metals could be remobilised from sediments and floodplain soils. Considering the remobilisation process, changes in pH-value and redox potential are most important (Foster and Charlesworth 1996, Calmano et al. 2005). This becomes largely apparent in floodplain soils where regularly fluctuating water levels lead to fluctuating redox conditions, which influence the mineralization of organic matter and affect the mobility of metals in soil. Moreover, the bioavailability of metals is influenced by the changing physico-chemical conditions in soils as well as by changes in flooding frequency. However, the quantification of metal mobilization on the basis of changing geochemical conditions is still lacking and even if several laboratory studies have examined the processes of adsorption and desorption of trace metals in soils, it still remains difficult to apply these results in the field. However, Table 2.6 gives an overview, without the demand of completeness, about the main trace metals within the Elbe floodplains and the factors influencing their mobility in soils. But above, mobile amounts of metals alone in the soil solution do not indicate to which amount mobilised metals will be transported to water bodies or to plants and consequently the toxicological effect of metal release. This is because of the complex determination of transfer and translocation processes of trace metals through floodplain soils primarily due to a high spatial variability of soil conditions, metal contamination, and the mobility of metals in soil, as well as of plant community composition. Thus notably predicting the actual soil-plant transfer and the contamination of green fodder in floodplains is uncertain and yet insufficient for legal action, because metal transfer into plants shows high element and plant specific differences (Krueger and Groengroeft 2004, Overesch et al. 2007). Besides, for the investigation of transport and translocation of trace metals in floodplain soils, basic prerequisites are the determination of groundwater recharge, the capillary ascent, the evapotranspiration as well as changes in the storage function of the soils (Meissner et al. 2000, Schwartz 2001). These parts of the soil water balance however are not directly measurable and can only be registered by assumptions using indirect factors, although lysimeters have been developed as instruments for a detailed and accurate investigation of soil water factors.

*Table 2.6* *Factors affecting the mobility and availability in soils and floodplains soils of the most important trace metals concerning the river Elbe floodplains ([1]laboratory studies, [2]field studies, [3]lysimeter studies; grey: general applicable for soils)*

| | Redox potential | Dissolved organic matter | Soil pH-value | Hydrous oxides | Clay content | Plant uptake |
|---|---|---|---|---|---|---|
| | Considering the remobilisation of heavy metals from sediment changes in **redox potential** and pH are most important (Calmano et al. 2005) | Dominant mechanism concerning metal mobility in wetland soils (Grybos et al. 2007)[1] | Considering the remobilisation of heavy metals from sediment changes in redox potential and **pH** are most important (Calmano et al. 2005) | Important in controlling metal mobility in wetland soils (Grybos et al. 2007)[1] | | Trace metal concentration in grassland vegetation of river Elbe floodplains are generally low and seldom correspond to stock in soils (Krueger & Groengroeft 2004)[2] |
| **Cd** | Highly mobile, which may lead to groundwater pollution and high bioavailiability at Cd contaminated sites (Lair et al. 2008)[2] | | | | | |
| | Greatly reduced solubility of Cd under anaerobic conditions, may due to precipitation of CdS (Reddy & Patrick 1977)[1] | Mobilisation depends <u>not</u> on DOM (Kalbitz & Wennrich 1998)[3] | Soil pH governed Cd distribution in investigated Elbe soils (Eisenmann 2002[2], Lair et al. 2008)[12]<br><br>Most important single soil property that determines Cd availability to plants (summed by Adriano 1986) | Fe-oxides with influence on adsorption (Dong et al. 2005)[2]<br><br>One important process is the sorption to hydrous Al, Fe and Mn oxides (Trivedi & Axe 2000)[1] | Higher sorption capacity in soils high in clay content (summed by Adriano 1986) | Highly phytoavailable restricted to soil horizons with pH<5.0 (Overesch et al. 2007)[2]<br><br>Even in cases of low amount of mobile Cd (0.1mg/kg), contents in plants were above critical values (Groengroeft et al. 2005)[2] |
| **As** | As mobilisation in floodplain soils was low (Kalbitz & Wennrich 1998) | | | | | |
| | Known as redox sensitive, its fate depends on oxidation status (summed Voegelin et al. 2007) | As concentration in soils positively correlated with DOM (Kalbitz & Wennrich 1998)[3] | Adsorption of As from solution was maximal at about pH 5 (summed by Adraino 1986) | Fe-Mn-Al-oxides effective sorbents of As(III) and As(IV) in soils; for the floodplain Muldenstein it is estimated that half of the As in the rooted | Effective sorbents for As(III) and As(IV)in soils (summed by Voegelin et al. 2007)[1] | Association of As with Fe-(hydr)oxides in the rhizosphere and the Fe-plaque may reduce the availability of As for plant uptake; massive accumulation of As close to the plant |

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| | | | | subsoil is associated with Fe(hydr)oxides enriched in the rhizosphere (Voegelin et al. 2007)[1] | | roots may increase As uptake by plants (summed by Voegelin et al. 2007)<br><br>Uptake seems to be enhanced on long submerged soils (Overesch et al. 2007)[2] |
| **Pb** | Reducing conditions lead to an increased mobility of Pb (Charlatchka & Cambier 2000)[1] | DOM more important as a sink than Fe-oxyhydroxides (Grybos et al. 2007[1], Van Griethuysen et al. 2005[2]) | Soil reaction probably the single most impritant factor affecting solubility, mobility, and phytoavailability (Adriano 1986) | Metal relase due to the combined effect of DOM release and Fe (III) reduction (Grybos et al. 2007)[1]<br><br>Mn-oxides with influence on adsorption (Dong et al. 2005)[2] | Al Fe-Mn-(hydr)oxides can play an important role in the sorption of Pb (summed by Adriano 1986) | Risk for uptake by herbage increases during the summer months (Overesch et al. 2007) [2]<br><br>It is assumed that the leaf-soil contact and dust impact is most important (Groengroeft et al. 2005)[2] |
| **Cu** | | | Strongly bound if existing (Graf et al. 2007)[2]: | | | |
| | Retention/re-mobilisation also affected by changes in redox state (Grybos et al. 2007)[1] | DOM seemed to be most important for Cu behavior in floodplain soils (Van Griethuysen 2005, Lair et al. 2008)[2] | pH-value > 5.0<br><br>pH strongly determined retention capacity (Graf et al. 2007)[2] | and high content of Fe-oxyhydroxides | and high clay content | |
| **Cr** | Retention/re-mobilisation also affected by changes in redox state (Grybos et al. 2007) [1]<br><br>Known as redox sensitive (Masscheleyn et al. 1992)[2] | DOM as an important sink (Van Griethuysen et al. 2005) [2] but not quantifiable due to the precipitation or re-adsorption of reduced phases (Grybos et al. 2007) [1] | Affects the solubility of the Cr forms and thus its sorption by soil and availability to plants (Adriano 1986) | Mn oxides and to a lesser content Fe oxides are very important in the adsorption of Cr by sediments (summed by Adriano 1986) | | In culture solutions absorbed Cr remained primarily in the roots and is poorly translocated (summed by Adriano 1986) |

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| **Hg** | Overall Hg mobilisation from the Elbe floodplain soils can be assumed to be low due to intensive interaction with OM (Wallschläger et al. 1998)[1] | | | | | |
| | Great rate of production of methymercury under reducing conditions; increased soil moisture lead to increased sorption of Hg vapor; redox potential also influences the stability of solid phases of Hg (summed by Adriano 1986) | Humic substances play most important part in binding Hg in river's floodplains compared with the corresponding sediments (Wallschlaeger et al. 1998)[1] | pH can affect the speciation and stability of Hg in the soil environment (Adriano 1986) | Fe-Mn-(hydro)oxides and clay minerals are not significant binding partners for Hg (Wallschläger et al. 1998)[1] | | Uptake seems to be enhanced on long submerged soils; risk for uptake by herbage increases with increasing temperatures (Overesch et al. 2007)[2] |
| **Ni** | | DOM more important as a sink than Fe-oxyhydroxides (Grybos et al. 2007) [1] | Increasing retention with increasing pH-values (summed by Adriano 1986) | Metal release due to the combined effect of DOM release and Fe (III) reduction (Grybos et. al. 2007)[1] | Higher Ni content in soils with decreasing particle size (summed by Adriano 1986) | High phytoavailability restricted to soil horizons with pH<5.0 (Overesch et al. 2007)[2] |
| **Zn** | Redox conditions with pronounced effect on the solubility of Zn; in constantly flooded soils relatively insoluble ZnS may be formed under strongly reduced conditions (summed by Adriano 1986) | Mobilisation depends not on DOM (Kalbitz & Wennrich 1998)[3] | Most soluble and hence phytoavailable under acidic conditions (summed by Adriano 1986) | One important process is the sorption to hydrous Al, Fe and Mn oxides (Trivedi & Axe 2000)[1] | | High phytoavailability restricted to soil horizons with pH<5.0 (Overesch et al. 2007)[2] |

However, with the currently existing technical measurements, a separation of the soil solution is not possible and thus the transport of mobile pollutants through the soil solution to other water bodies is not quantifiable so far. It is therefore advisable to combine different measurement systems as in situ investigations like soil water stations in the field or tracer analysis together with lysimeter studies to detect the transport of pollutants on floodplain study sites (Bethge-Steffens 2008). Since the transport of several trace metals in rivers is directly linked to the transport of suspended particulate matter and sediments, it is essential to know the dynamics of the sediment transport in the system including the sources, pathways and in-between storage of sediments for monitoring and modelling the behaviour of pollutants in river systems (Friese 2006). This is of particular concern according to the requirements of the EU Water Framework Directive (European Commission, 2000), but also if management suggestion are necessary particularly in the case of land use modifications or during remediation activities. So far it is still highly complicated to announce general advices concerning the management of polluted floodplains notably because of the great variability of metal concentration in time and space. However, Groengroeft et al. (2005) summarise that particularly after flood events grazing should be discontinued. Further, flood channels and depression revealing highest contaminations and/or phyto-availabilities should be precluded from grazing and instead only used for mown grass (Overesch et al. 2007), since grazing animals may also take up significant amounts of trace metals by inhalation and ingestion of contaminated soils (Thornton and Abrahams 1983). Consequently, floodplain areas, besides other structures within a river catchment like groin fields, still need to be considered when studying the role and behaviour of sediments for the transport of pollutants within river systems as well as the effects mobile trace metals may have on the food chain.

Acknowledgments

This paper has been written within the EU-project Eurolimpacs (EU Contract no. GOCE-CT-2003-505540). We want to thank Volker Eisenmann and Rene Schwartz for providing data and Hans Middelkoop for recommending additional literature. Further, we strongly appreciate the very helpful comments of our colleagues from the Department of Conservation Biology and Soil Physics at the Helmholtz Centre for Environmental Research (UFZ) during the completion of this work. Two reviewers are acknowledged for their useful comments on this paper. Furthermore, we thank Sarah Gwillym for proofreading the manuscript.

## References


Adams, D.D., 1994. Sediment pore water sampling. pp. 171–202. In: M.S. Murdoch and S.D. Macknight (ed.) Handbook of techniques for aquatic sediments sampling. Lewis Publ., Boca Raton, FL.

Adams, M.S., Kausch, H., Gaumert, T. Kruger, K.E., 1996. The effect of the reunification of Germany on the water chemistry and ecology of selected rivers. Environmental Conservation 23:35–43.

Adriano, D.C., 1986. Trace elements in the terrestrial environment. Springer, New York.

Adriano, D.C., 2001. Biogeochemical processes regulating metal behavior. pp. 30–59. In: D.D Adriano (ed.) Trace elements in terrestrial environments: Biogeochemistry, bioavailability and risks of metals. Springer, New York.

Albering, H., Van Leusen, S.M., Moonen, E.J.C., Hoogewerff, J.A., Kleinjans, J.C.S., 1999. Human health risk assessment: A case study involving heavy metal soil contamination after the fl ooding of the River Meuse during the winter of 1993–1994. Environmental Health Perspectives 107:37–43.

Alloway, B.J., 1997. The mobilisation of trace elements in soils. pp. 133–145. In: R. Prost (ed.) Contaminated Soils, Proceedings of the 3rd International Conference on the Biogeochemistry of Trace Elements, Paris. 15–19 May 1995. INRA, Paris.

ARGE-Elbe (Arbeitsgemeinschaft zur Reinhaltung der Elbe), 1982–2005. Tables of monitoring measurements. *Available at www.arge-elbe.de/wge/Download/DDaten.php (verified 23 Mar. 2009).*

Baldwin, D.S., Mitchell, A.M., 2000. The effects of drying and re-flooding on the sediment and soil nutrient dynamics of lowland river-floodplain systems: A synthesis. Regulated Rivers: Research and Management 16:457–467.

Barona, A., Romero, F., 1997. Relationships among metals in the solid phase of soils and in wild plants. Water Air and Soil Pollution 95:59–74.

BBodSchV. 1999. BGBl. I S. 1554, Stand: Geandert durch Art. 2 V v.23.12.2004 I 3758.

Berner, R., 1980. Early diagenesis: A theoretical approach. Princeton Univ. Press, Princeton, NJ.

Bethge-Steffens, D., 2008. Der Bodenwasserhaushalt von zwei reprasentativen Flussauenstandorten der Mittelelbe, Untersuchungen mit wägbaren Grundwasserlysimetern, UFZ-Diss. 1/2008, Leipzig. PhD.

BfG (Federal Institute of Hydrology). 2002. Das Augusthochwasser 2002 im Elbegebiet. Koblenz. *Available at http://www.meteo.uni-koeln.de/ content/downloads/elbe2002.pdf (verified 25 Mar. 2009).*

Blume, H.P., Bruemmer, G., 1991. Prediction of heavy-metal behavior in soil by means of simple field-tests. Ecotoxicolgy and Environmental Safety 22:164–174.

Brack, W., Klamer, H.J.C., de Ada, M.L. Barcelo, D., 2007. Effect-directed analysis of key toxicants in European river basins–A review. Environmental Science and Pollution Research 14:30–38.

Brallier, S., Harrison, R.B., Henry, C.L., Dongsen, X., 1996. Liming effects on availability of Cd, Cu, Ni and Zn in a soil amended with sewage sludge 16 years previously. Water Air and Soil Pollution 86:195–206.

Bruemmer, G.W., Gerth, J., Herms, U., 1986. Heavy metal species, mobility and availability in soils. Zeitschrift für Pflanzenernährung und Bodenkunde 149:382–398.

Burton, G.A., 1992. Assessing contaminated aquatic sediments. Environmental Science and Technology 26:1862–1863.

Calmano, W., Hong, J., Foerstner, U., 1993. Binding and mobilization of heavy-metals in contaminated sediments affected by pH and redox potential. Water Science and Technology 28:223–235.

Calmano, W., von der Kammer, F., Schwartz, R., 2005. Characterization of redox conditions in soils and sediments: Heavy metals. IWA Publication, London, UK

Charlatchka, R., Cambier, P., 2000. Influence of reducing conditions on solubility of trace metals in contaminated soils. Water Air and Soil Pollution 118:143–167.

Chuan, M., Shu, G., Liu, J., 1996. Solubility of heavy metals in contaminated soil: Effects of redox potential and pH. Water Air and Soil Pollution 90:543–556.

Ciszewski, D., Czajka, A., Blazej, S., 2008. Rapid migration of heavy metals and 137Cs in alluvial sediments, Upper Odra River valley, Poland. Environmental Geology 55:1577–1586.

Davies, B.E., 1992. Interrelationships between soil properties and the uptake of cadmium, copper, lead and zinc from contaminated soils by radish (Raphanus sativus L). Water Air and Soil Pollution 63:331–342.

Davranche, M., Bollinger, J.C., 2000a. Heavy metals desorption from synthesized and natural iron and manganese oxyhydroxides: Effect of reductive conditions. Journal of Colloid Interface Science 227:531–539.

Davranche, M., Bollinger, J.C., 2000b. Release of metals from iron oxyhydroxides under reductive conditions: Eff ect of metal/solid interactions. Journal of Colloid Interface Science 232:165–173.

Dong, D.M., Yang, F., Yu, L., Hua, X.Y., Lu, X.J., Zhang, J.J., 2005. Adsorption of Pb, Cd to Fe-, Mn oxides in natural freshwater surface coatings developed in different seasons. Journal of Environmental Science (China) 17:30–36.

Duft, M., Tillmann, M., Oehlmann, J., 2003. Okotoxikologische Sedimentkartierung der großen Flüsse Deutschlands. UBA-Texte, 26/03. Berlin. *Available at http://www.bio-inf.uni-frankfurt.de/ee/ecotox/_files/publications/UBA-Sediment%20Abschlussbericht.pdf (verified 25 Mar. 2009).*

Duve, J., 1999. Bilanzierung des Stoffaustausches zwischen Elbe und Deichvorland am Beispiel zweier Tidebeeinflusster Untersuchungsgebiete. Hamburger Bodenkundliche Arbeiten, 43, PhD.

Eisenmann, V., 2002. Die Bedeutung der Böden fur das Renaturierungspotential von Rückdeichungsgebieten an der mittleren Elbe. Hamburger Bodenkundliche Arbeiten, 51, Ph.D.

Engel, H., 2004. The flood event 2002 in the Elbe river basin, causes of the flood, its course, statistical assessment and flood damages. Houille Blanche-Revue Internationale De L Eau 6:33–36.

European Commission., 2000. Directive 2000/60/EC of the European parliament and of the office council of 23 October 2000 establishing a framework for Community action in the field of water policy (Water Framework Directive) Official Journal of the European Communities. L327. 1-72. Brussels.

European Environment Agency., 1995. Europe's environment–The Dobris assessment. Earthscan Publications. Copenhagen.

Fergusson, J., 1990. The heavy elements, chemistry, environmental impact and health eff ects. Pergamon Press, Oxford.

Fittschen, R., Groengroeft, A., 2000. Eisen- und Manganverteilung in eingedeichten Auenböden der Mittelelbe. pp. 79–88. In: K. Friese et al. (ed.) Stoffhaushalt von Auenökosystemen. Böden, Hydrologie, Schadstoffe, Bewertungen. Springer, Berlin.

Foster, I.D.L., Charlesworth, S.M., 1996. Heavy metals in the hydrological cycle: Trends and explanation. Hydrological Processes 10:227–261.

Friese, K., 2006. Floodplains and areas of low water movement as the linking part in the transport of suspended particulate matter and sediments along lowland rivers. Acta Hydrochimica et Hydrobiologica 34:171–173.

Gambrell, R.P., 1994. Trace and toxic metals in wetlands–A review. Journal of Environmental Quality 23:883–891.

Gambrell, R.P., Collard, V., Patrick, W. Jr., 1980. Cadmium uptake by marsh plants as aff ected by sediment physicochemical conditions. pp. 425–444. In: R.A. Baker (ed.) Contaminants and sediments. Ann Arbor Science.

Gambrell, R.P., DeLaune, R., Patrick, W. Jr., 1991a. Redox processes in soils following oxygen depleting. pp. 101–117. In: M.B. Jackson et al. (ed.) Plant life under oxygen deprivation. SpB Academic Publication, The Hague.

Gambrell, R.P., Patrick, W. Jr., 1988. The influence of redox potential on the environmental chemistry of contaminants in soils and sediments. pp. 319–333. In: D.D. Hook (ed.) The ecology and management of wetlands. Timber Press, Portland, OR.

Gambrell, R.P., Wiesepape, J.B., Patrick, W.H., Duff, M.C., 1991b. The effects of pH, redox, and salinity on metal release from a contaminated sediment. Water Air and Soil Pollution 57:359–367.

Geller, W., Ockenfeld, K., Böhme, M., Knöchel, A. (ed.), 2004. Schadstoffbelastung nach dem Elbe-Hochwasser 2002, Endbericht des Adhoc-Projekts: Schadstoffuntersuchungen nach dem Hochwasser vom August 2002, Ermittlung der Gefährdungspotentiale an Elbe und Mulde. BMBF Forderkennzeichen PTJ 0330492 KDD, Nürnberg.
*Available at http:// www.ufz.de/hochwasser/bericht/HWEnd.pdf (verified 25 Mar. 2009).*

Graf, M., Lair, G.J., Zehetner, F., Gerzabek, M.H., 2007. Geochemical fractions of copper in soil chronosequences of selected European floodplains. Environmental Pollution 148:788–796.

Groengroeft, A., Krueger, F., Grunewald, K., Meissner, R., Miehlich, G., 2005. Plant and soil contamination with trace metals in the Elbe floodplains: A case study after the flood in August 2002. Acta Hydrochimica et Hydrobiologica 33:466–474.

Grybos, M., Davranche, M., Gruau, G., Petitjean, P., 2007. Is trace metal release in wetland soils controlled by organic matter mobility or Feoxyhydroxides reduction? Journal of Colloid Interface Science 314:490–501.

Hamilton-Taylor, J., Davison, W., 1995. Redox-driven cycling of trace elements in lakes. pp. 217–263. In: A. Lerman et al. (ed.) Physics and chemistry of lakes. Springer, Berlin.

Harres, H.P., 1998. Schwermetallgehalte in Böden, Pflanzen, Fließgewässern und Sedimenten unterschiedlich belasteter Regionen Südsardiniens. Untersuchungen zur regionalen

Differenzierung und zeitlichen Veränderung sowie zur geoökologischen Relevanz von Schwermetallverlagerungen. University of Halle/Saale, Germany. Habilitation.

Harter, R.D., Naidu, R., 2001. An assessment of environmental and solution parameter impact on trace-metal sorption by soils. Soil Science Society of America Journal 65:597–612.

Heinrich, K., Rinklebe, J., Neue, H.-U., 2000. Einflus des heißwasserlöslichen Kohlenstoffs auf Redoxpotentialänderungen während simulierter Hochwassereignisse. pp. 47–54. In: K. Friese et al. (ed.) Stoffhaushalt von Auenökosystemen-Boden, Hydrologie, Bewertungen. Springer, Berlin.

Herms, U., Bruemmer, G., 1984. Solubility and retention of heavy-metals in soils. Zeitschrift für Pflanzenernährung und Bodenkunde 147(3):400–424.

Hobbelen, P.H.F., Koolhaas, J.E., Van Gestel, C.A.M., 2004. Risk assessment of heavy metal pollution for detritivores in floodplain soils in the Biesbosch, the Netherlands, taking bioavailability into account. Environmental Pollution 129:409–419.

Hoehn, A., Hierold, W., Prietzsch, C., Schalitz, G., 2000. Schwermetallverteilung in Auenböden des Nationalparks Unteres Odertal. pp. 359–368. In: K. Friese et al. (ed.) Stoffhaushalt von Auenökosystemen-Boden, Hydrologie, Bewertungen. Springer, Berlin.

Jenne, E.A., 1968. Controls on Mn, Fe, Co, Ni, Cu and Zn concentrations in soils and water, significant role of hydrous Mn and Fe oxides. Advances in Chemistry Series 73:337–387.

Junk, W., Bayley, P., Sparks, R., 1989. The flood pulse concept in river floodplain systems. Canadian Journal of Fisheries and Aquatic Science 106:110–127.

Kabata-Pendias, A., 2001. Trace elements in soils and plants. CRC Press, Boca Raton, FL.

Kalbitz, K., Knappe, S., 1997. Influence of soil properties on the release of dissolved organic matter (DOM) from the topsoil. Zeitschrift für Pflanzenernährung und Bodenkunde 160(5):475–483.

Kalbitz, K., Wennrich, R., 1998. Mobilization of heavy metals and arsenic in polluted wetland soils and its dependence on dissolved organic matter. Science of the Total Environment 209:27–39.

Klemm, W., Greif, A., Broekaert, J.A.C., Junge, F.W., Van der Veen, A., Schultze, M., Duffek, A., 2005. A study on arsenic and the heavy metals in the Mulde river system. Acta Hydrochimica et Hydrobiologica 33(5):475–491.

Kooistra, L., Leuven, R., Nienhuis, P.H., Wehrens, R., Buydens, L.M.C., 2001. A procedure for incorporating spatial variability in ecological risk assessment of Dutch River floodplains. Environmental Management 28:359–373.

Krueger, A., Neumeister, H., 1999. Schadstoffmobilisierung und Verteilung in Flussauen, Auswirkungen der Veränderungen des geochemischen Milieus nach künstlicher Uberflutung und Grundwasseranstieg. pp. 23–38 In: A. Groengroeft and R. Schwartz (ed.) Eigenschaften und Funktionen von Auenboden an der Elbe. Hamburger Bodenkundliche Arbeiten, 44.

Krueger, F., Groengroeft, A., 2004. The difficult assessment of heavy metal contamination of soils and plants in Elbe river floodplains. Acta Hydrochimica et Hydrobiologica 31:436–443.

Krueger, F., Groengroeft, A., Grunewald, K., Meisner, R., Miehlich, G., Petzold, H., Unger, C., 2004b. Auswirkungen der Schadstoffgehalte und Keimbelastung von Hochflutsedimenten auf Böden und Pflanzen. pp. 224–286. In: P. Geller et al. (ed.) Schadstoffbelastung nach dem Elbe Hochwasser 2002, Endbericht des Ad-hoc-Projekts: Schadstoffuntersuchungen nach dem Hochwasser vom August 2002-Ermittlung der Gefahrdungspotentiale an Elbe und Mulde.
*Available at htth://www.ufz.de/hochwasser/bericht/HWEnd.pdf (verified 25 Mar. 2009).*

Krueger, F., Meissner, R., Groengroeft, A., Grunewald, K., 2005. Flood induced heavy metal and arsenic contamination of Elbe river floodplain soils. Acta Hydrochimica et Hydrobiologica 33:455–465.

Krueger, F., Prange, A., Jantzen, E., 1999. Ermittlung geogener Hintergrundwerte an der Mittelelbe und deren Anwendung in der Beurteilung von Unterwassersedimenten. pp. 39–51. In: A. Groengroeft and R. Schwartz (ed.) Eigenschaften und Funktionen von Auenboden an der Elbe. Hamburger Bodenkundliche Arbeiten 44.

Kuntze, H., Herms, U., 1986. Bedeutung geogener und pedogener Faktoren fur die weitere Belastung der Boden mit Schwermetallen. Naturwissenschaften 73:195–205.

Kuntze, H., Herms, U., Pluquet, E., 1984. Schwermetalle in Boden-Bewertung und Gegenmaßnahmen. Geologische Jahrbücher. Reihe A. 75:715–736.

Lair, G.J., Graf, M., Zehetner, F., Gerzabek, M.H., 2008. Distribution of cadmium among geochemical fractions in floodplain soils of progressing development. Environmental Pollution 156:207–214.

Lindsay, W., 1979. Chemical equilibria in soils. John Wiley & Sons, New York.

Masscheleyn, P.H., Pardue, J.H., Delaune, R.D., Patrick, W.H., 1992. Chromium Redox Chemistry In A Lower Mississippi Valley Bottomland Hardwood Wetland. Environmental Science and Technology 26:1217–1226.

Matagi, S.V., Swai, D., Mugabe, R., 1998. A review of heavy metal removal mechanisms in wetlands. African Journal of Tropical Hydrobiology and Fisheries 8:23–35.

Meissner, R., Rupp, H., Schubert, M., 2000. Novel lysimeter techniques. A basis for the improved investigation of water, gas, and solute transport in soils. Journal of. Plant Nutrient and Soil Science 163:603–608.

Meybeck, M., Lestel, L., Bonte, P., Moilleron, R., Colin, J.L., Rousselot, O., Herve, D., de Ponteves, C, Grosbois, C., Thevenot, D.R., 2007. Historical perspective of heavy metals contamination (Cd, Cr, Cu, Hg, Pb, Zn) in the Seine River basin (France) following a DPSIR approach (1950–2005). Science of the Total Environment 375:204–231.

Middelkoop, H., 2000. Heavy-metal pollution of the river Rhine and Meuse floodplains in the Netherlands. Geologie En Mijnbouw/Netherlands Journal of Geosciences 79:411–427.

Mueller, H.W., Schwaighofer, B., Kalman, W.,1994. Heavy-metal contents in river sediments. Water Air and Soil Pollution 72:191–203.

Negrel, P., 1997. Multi-element chemistry of Loire estuary sediments: Anthropogenic vs. natural sources. Estuarine Coastal Shelf Sciences 44:395–410.

Ng, S., Bloomfield, C., 1962. The eff ect of flooding and aeration on the mobility of certain trace elements in soils. Plant and Soil´6:108–135.

O'Halloran, K., 2006. Toxicological considerations of contaminants in the terrestrial environment for ecological risk assessment. Human and Ecological Risk Assessment 12:74–83.

Olivie-Lauquet, G., Gruau, G., Dia, A., Riou, C., Jaffrezic, A., Henin, O., 2001. Release of trace elements in wetlands: Role of seasonal variability. Water Research 35:943–952.

Overesch, M., Rinklebe, J., Broll, G., Neue, H.-U., 2007. Metals and arsenicin soils and corresponding vegetation at Central Elbe river floodplains (Germany). Environmental Pollution 145:800–812.

Peijnenburg, W., Jager, T., 2003. Monitoring approaches to assess bioaccessibility and bioavailability of metals: Matrix issues. Ecotoxicology and Environmental Safety 56:63–77.

Pierzynski, G., 1994. Soils and environmental quality. Taylor and Francis, Boca Raton, FL.

Poot, A., Gillissen, F., Koelmans, A.A., 2007. Effects of flow regime and flooding on heavy metal availability in sediment and soil of a dynamic river system. Environmental Pollution 148:779–787.

Qu, W.C., Kelderman, P., 2001. Heavy metal contents in the Delft canal sediments and suspended solids of the River Rhine: Multivariate analysis for source tracing. Chemosphere 45:919–925.

Rate, A.W., Robertson, A.E., Borg, A.T., 2000. Distribution of heavy metals in near-shore sediments of the Swan River estuary, Western Australia. Water Air and Soil Pollution 124:155–168.

Reddy, K.R., Patrick, W.H., 1975. Effect of alternate aerobic and anaerobic conditions on redox potential, organic matter decomposition and nitrogen loss in a flooded soil. Soil Biology and Biochemistry 7:87–94.

Reddy, K.R., Patrick, W.H., 1977. Eff ect of redox potential and pH on the uptake of cadmium and lead by rice plants. Journal of Environmental Quality 6:259–262.

Rieuwerts, J.S., Thornton, I., Farago, M.E., Ashmore, M.R., 1998. Factors influencing metal bioavailability in soils: Preliminary investigations for the development of a critical loads approach for metals. Chemical Speciation and Bioavailability 10:61–75.

Rinklebe, J., Franke, C., Neue, H.-U., 2007. Aggregation of floodplain soils based on classification principles to predict concentrations of nutrients and pollutants. Geoderma 141:210–223.

Scheffer, F., Schachtschabel, P., 2002. Lehrbuch der Bodenkunde. Spectrum, Heidelberg.

Schipper, A.M., Wijnhoven, S., Leuven, R., Ragas, A.M.J., Hendriks, A.J., 2008. Spatial distribution and internal metal concentrations of terrestrial arthropods in a moderately contaminated lowland floodplain along the Rhine River. Environmental Pollution 151:17–26.

Scholten, M., Anlauf, A., Buechele, B., Faulhaber, P., Henle, K., Kofalk, S., Leyer, I., Meyerhoff, J., Purps, J., Rast, G., Scholz, M., 2005. The River Elbe in Germany present state, conflicting goals, and perspectives of rehabilitation. Large Rivers 15:579–602.

Schwartz, R., 2001. Die Böden der Elbaue bei Lenzen und ihre möglichen Veränderungen nach Rückdeichung. Hamburger Bodenkundliche Arbeiten. 48, Ph.D.

Schwartz, R., Gerth, J., Neumann-Hensel, H., Bley, S., Foerstner, U., 2006. Assessment of highly polluted fluvisol in the Spittelwasser floodplain. Based on national guideline values and MNA-Criteria. Journal of Soils and Sediments 6:145–155.

Schwartz, R., Groengroeft, A., Miehlich, G., 2004. Pore water composition as device for the detection of origin and fl ow direction of soil water in alluvial soils of the Middle Elbe River. Acta Hydrochimica et Hydrobiologica 31:423–435.

Schwartz, R., Schmidt, B., Miehlich, G., 1998. Einfluß einer Hochwasserwelle auf den Wassergehalt und das Redoxpotential von Auenboden an der Mittelelbe. pp. 257–258. In: P. Geller et al. (ed.) Gewässerschutz im Einzugsgebiete der Elbe. Teubner, Leipzig.

Shaw, T.J., Gieskes, J.M., Jahnke, R.A., 1990. Early diagenesis in differing depositional environments. The response of transition-metals in pore water. Geochimica et Cosmochimica Acta 54:1233–1246.
Shiller, A.M., 1997. Dissolved trace elements in the Mississippi river: Seasonal, interannual, and decadal variability. Geochimica et Cosmochimica Acta 61:4321–4330.
Sims, J.L., Patrick, P.H., 1978. Distribution of micronutrient cations in soil under conditions of varying redox potential and pH. Soil Science Society of America Journal 42:258–262.
Sims, J.T., 1986. Soil-pH eff ects on the distribution and plant availability of manganese, copper, and zinc. Soil Science Society of America Journal 50:367–373.
Soares, H., Boaventura, R.A.R., Machado, A., da Silva, J., 1999. Sediments as monitors of heavy metal contamination in the Ave river basin (Portugal): Multivariate analysis of data. Environmental Pollution 105:311–323.
Song, Y.G., Mueller, G., 1995. Biogeochemical cycling of nutrients and trace-metals in anoxic fresh-water sediments of the Neckar River, Germany. Marine and Freshwater Research 46:237–243.
Tack, F.M.G., Van Ranst, E., Lievens, C., Vandenberghe, R.E., 2006. Soil solution Cd, Cu and Zn concentrations as affected by short-time drying or wetting. The role of hydrous oxides of Fe and Mn. Geoderma 137:83–89.
Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace-metals. Analytical Chemistry 51:844–851.
Thonon, I., 2006. Deposition of sediment and associated heavy metals on floodplains. Utrecht Univerisity. Netherlands Geographical Studies 337, Ph.D.
Thornton, J., Abrahams, P., 1983. Soil ingestion. A major pathway of heavy metals into livestock grazing on contaminated land. Science of the Total Environment 28:139–151.
Tockner, K., Malard, F., Ward, J.V., 2000. An extension of the flood pulse concept. Hydrological Processes 14:2861–2883.
Trivedi, P., Axe, L., 2000. Modeling Cd and Zn sorption to hydrous metal oxides. Environment Science and Technology 34:2215–2223.
Turner, J.N., Brewer, P.A., Macklin, M.G., 2008. Fluvial controlled metal and As mobilisation, dispersal and storage in the Rio Guadiamar, SW Spain and its implications for long-term contaminant fluxes to the Donana wetlands. Science of the Total Environment 394:144–161.
Van den Berg, G.A., 1998. Geochemical behaviour of heavy metals in a sedimentation area of the rivers Rhine and Meuse. Utrecht University. Geologica Ultraiectina 163, Ph.D.
Van den Berg, G.A., Loch, J.P.G., Van der Heijdt, G., Lambertus, M., Zwolsmann, J.J.G., 2000. Geochemical behaviour of trace metals in freshwater sediments. p. 517–533. In: B. Markert and K. Friese (ed.) Trace elements. Their distribution and eff ects in the environment. Elsevier, Amsterdam.
Van der Veen, A., Ahlers, C., Zachmann, D.W., Friese, K., 2006. Spatial distribution and bonding forms of heavy metals in sediments along the middle course of the River Elbe (km 287. 390). Acta Hydrochimica et Hydrobiologica 34:214–222.
Van Griethuysen, C., Luitwieler, M., Joziasse, J., Koelmans, A.A., 2005. Temporal variation of trace metal geochemistry in fl oodplain lake sediment subject to dynamic hydrological conditions. Environmental Pollution 137:281–294.
Voegelin, A., Weber, F.A., Kretzschmar, R., 2007. Distribution and speciation of arsenic around roots in a contaminated riparian floodplain soil: Micro-XRF element mapping and EXAFS spectroscopy. Geochimica et Cosmochimica Acta 71:5804–5820.
Vogt, M., Zachmann, D., Treutler, C., Krueger, F., Friese, K., 2000. Zeitliche Belastungsentwicklung von Sedimenten aus Elbaue-Stillgewässern. pp. 209–217. In: K. Friese et al. (ed.) Stoffhaushalt von Auenökosystemen. Böden, Hydrologie, Schadtsoffe, Bewertungen. Springer, Berlin.
Wallschlaeger, D., Desai, M.V.M., Spengler, M., Wilken, R.D., 1998. Mercury speciation in floodplain soils and sediments along a contaminated river transect. Journal of Environmental Quality 27:1034–1044.
Xian, X.F., Shokohifard, G.I., 1989. Effect of pH on chemical forms and plant availability of cadmium, zinc, and lead in polluted soils. Water Air and Soil Pollution 45:265–273.
Xiong, L.M., Lu, R.K., 1993. Effect of liming on plant accumulation of cadmium under upland or flooded conditions. Environmental Pollution 79:199–203.
Youssef, R.A., Chino, M., 1991. Movement of metals from soil to plantroots. Water Air and Soil Pollution 57(8):249–258.
Zerling, L., Hanisch, C., Junge, F.W., 2006. Heavy metal inflow into the floodplains at the mouth of the river Weisse Elster (Central Germany). Acta Hydrochimica et Hydrobiologica 34:234–244.

Chapter 3

# Spatial and seasonal distribution of trace metals in floodplain soils.

# A case study with the Middle Elbe River, Germany

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*Geoderma 211-212:128–137 (2013)*

## Abstract

Field monitoring stations were used to assess selected soil parameters and trace metal concentrations in soil solution (As, Cd, Cu, Cr, Ni, Zn) to assess their behaviour under spatial as well as seasonal variations. We investigated three different plots within a floodplain research area varying in terms of their soil characteristics as well as their trace metal contents. Redox potential was found to be an important factor controlling the release of trace metals under field conditions on all plots coupled with a strong seasonal influence in almost all cases. However, by using generalised additive models it was possible to identify the specific courses of redox potentials related to the several trace metals depending on seasonal changes across the three plots. Whereas Cu and Cr concentrations increased with increasing redox potentials, Cd, Ni and Zn concentrations decreased. No clear pattern could be identified for As, although the data clearly reveal a seasonal dependency on flood events over the year and show increasing As concentrations even during smaller inundation events. The results of the generalised additive mixed models identified hot spots and hot moments of dissolved trace metal concentrations specific to soil horizons within the three plots. Thus we can provide data for further management implications that should be taken into account in an ecosystem that provides a whole host of ecosystem functions and services.

### 3.1 Introduction

Floodplains are one of the most important dynamic and heterogeneous ecosystems, showing complex patterns of diversity over a large range of temporal and spatial scales. These patterns occur from interactions between hydro-geomorphological and ecological processes such as natural disturbance and succession (Tockner et al. 2010). One main concept of understanding how floodplains develop and are maintained is the flood pulse concept (FPC) with its recent amplifications and derivatives. Tockner et al. (2010) suggested the pulsing of river discharge to be a major driving force that determines the degree of connectivity, the exchange of matter and the processing of organic matter and nutrients across river-floodplain gradients (Junk 2004, Thorp et al. 2006, Tockner et al. 2000). The FPC focuses on lateral and overland flood inundation and the relatively slow physical turnover rates of habitats. The FPC concept also plays an important role in terms of trace metal (TM) distribution in floodplain soils because flood events with river water, and thus occasional flood pulses, are the main source for TM input into floodplains (Zerling et al. 2006). This is crucial because since the industrial revolution (coupled with an increase in population density), rivers have faced several water quality problems. TM concentrations in rivers increased considerably in Europe during the 19th and 20th centuries. The river Elbe catchment area was no exception whereby intense and ongoing contamination even continued into the 1990s. However, even if harmful metal concentrations decreased in the river Elbe (tables of ARGE-Elbe, 1984–2000) and many western European rivers over recent decades, levels are still high compared to natural values (Mueller et al. 1994, EEA 1995, Negrel 1997, Soares et al. 1999, Qu and Kelderman 2001, Meybeck et al. 2007, Poot et al. 2007, Turner et al. 2008) and future target quality levels. Riverine floodplains can adopt water quality functions for rivers during periods of flooding but consequently river floodplains are usually heavily polluted with contaminants (see Schulz-Zunkel and Krueger 2009). Due to the fact that floodplains are, naturally, a complex mosaic of habitat patches, each slightly differing in productivity, standing biomass, soil organic content and capacity to transform organic matter (Tockner et al. 2010) and therefore displaying strong spatial as well as seasonal heterogeneity they can be both sinks and sources for TMs (Eisenmann 2002). The function of pollutant retention is very well known and has been researched by numerous authors for several floodplains (e.g. Middelkoop 2000, Hobbelen et al. 2004, Krueger and Groengroeft 2004, Ciszewski et al. 2008). Surprisingly, only few studies exist that investigates the release of TMs in floodplains under field conditions (Masscheleyn et al. 1992, Schwartz 2001, Eisenmann 2002, Dong et al. 2005, Van Griethuysen et al. 2005, Graf et al. 2007, Lair et al. 2008). In fact, it is mainly from laboratory studies that we are aware of how changes in soil biogeochemistry lead to TM release from floodplain soils. The redox processes that take place in combination with pH-value changes are the most important factors for retention and remobilisation triggered by hydrological conditions within floodplains and across river floodplain gradients (Schulz-Zunkel and Krueger 2009). However, laboratory results are very complex and it is difficult to specifically apply them within the field, because TM contents and fluxes in floodplains are often spatially and seasonally variable, mainly because of the biogeochemical processes that also vary in space and time. Particularly against the background of upcoming climate change and predicted seasonal shifts in floods and droughts, deeper knowledge is required to establish under which circumstances biogeochemical as well as transport hot spots and hot moments can also be identified in retaining or releasing TMs in floodplains. According to Vidon et al. (2010) biogeochemical hot spots in riparian zones are areas or patches that show disproportionately high reaction rates (greater than one order of magnitude higher) relative to the surrounding area (or matrix). Biogeochemical hot moments in riparian zones are short periods of time (<20% of the time) that show disproportionately high reaction rates relative to longer intervening time periods. Similarly, transport hot spots are areas or patches where solute fluxes are disproportionately higher (greater than one order of magnitude higher) than in surrounding areas. Transport hot moments are also short periods (<20% of the time) during which solute fluxes are significantly greater than during the intervening time. A comprehensive assessment of the role of hot spots and moments for a wide range of TMs, nutrients and contaminants is still lacking, however (Vidon et al. 2010). The purpose of this research was therefore to identify spatial as well as seasonal distribution patterns of dissolved TMs under changing biogeochemical conditions in floodplain soils using field monitoring stations under several assumptions: a) the most polluted plots show the highest dissolved amounts of TMs in the soil solution and thus biogeochemical and transport hot spots in floodplains, b) TM dissolution can be related to changes in soil biogeochemistry and indicated by soil parameters even under field conditions and c) seasonal changes appear at spatial as well as time scales thus we can identify scale dependent biogeochemical hot spots and hot moments.

## 3.2 Material and methods

### 3.2.1 Research area

The research area 'Schönberg Deich' is a floodplain along the German Middle Elbe region which is used as meadow and also for cattle. It is situated within a meander loop that encloses ca. 200 ha of a floodplain on the left side of the river Elbe (Fig. 3.1).

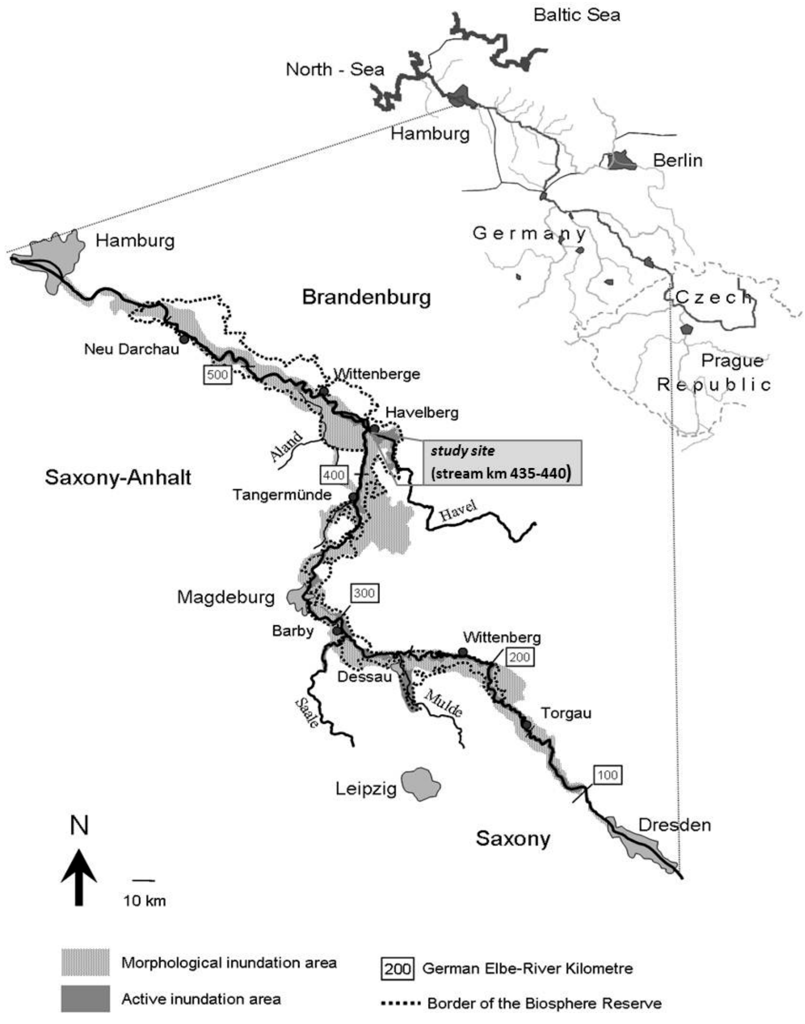



Figure 3.1 The river Elbe in Germany. (adapted from Scholten et al. 2005)

The Elbe itself is the third largest river of Central Europe, in terms of its length and the size of its catchment area. Discharge from the river Elbe is mainly influenced by snowmelt in spring. As a result high water levels mainly occur in spring (Scholten et al. 2005). As far as its process dynamics are concerned the river Elbe in Germany and its floodplains have remained semi-natural. Channelling of the Elbe has not taken place and only a few meanders have been straightened. It has, however, lost a majority of its floodplains. Those that do actually remain are regularly flooded and thus able to maintain the wetland and floodplain forest habitats that are unique within central Europe (after Adams et al. 2001). Also the research area 'Schönberg Deich' is flooded regularly in spring, though, due to divers micro-topography only during higher flood events the whole area is flooded. Within the research area site we identified three study plots that are typical hydro-geomorphological units within floodplains: levee, plateau and depression. Those plots also represent a topographical as well as pollution gradient from slightly (levee) via medium (plateau) to high (depression) flooding frequencies; flood duration and total TM content.

### 3.2.2 Soil sampling, pre-treatment and analysis of the sampled soils

Soils were collected horizon specific from the three plots. Soil material was homogenised, air-dried and sieved <2 mm. Soil properties were determined according to standard methods (Schlichting et al. 1995) as follows: Total C and N were measured with dry combustion and thermal conductivity detection using a C/N/S-Analyser (Vario EL Heraeus, Analytik Jena, Germany), pH-value was measured by an electrode (Dr. Lange, Germany).

*Table 3.1 Characteristics of the studied plots*

| studied plots | soil characteristics | | | | | | trace metals (mg/kg) *aqua regia dissolution* | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | masl[1] | H[5] | depth | pH (H$_2$0) | C (%) | N (%) | As (50) | Cd (20) | Cu (1300) | Cr | Ni (1900) | Pb (1200) | Zn |
| **levee** alluvial brown soil *(Vega)* of alluvial loamy sand | 24.9[2] | L1 | 10-25 | 3.96 | 1.068 | 0.092 | 18.3 | 0.4 | 22.5 | 21.0 | 16.6 | 43.3 | 76.0 |
| | | L2 | 25-50 | 4.49 | 0.579 | 0.065 | 14.1 | 0.7 | 15.9 | 20.1 | 27.0 | 27.1 | 96.0 |
| | | L3 | 50-75 | 4.88 | 0.274 | 0.030 | 8.7 | 0.4 | 9.0 | 12.1 | 16.7 | 19.1 | 55.0 |
| **plateau** alluvial brown soil *(Vega)* of alluvial loam | 24.3[3] | P1 | 20-50 | 6.6 | 0.6 | 0.058 | 13.5 | 0.6 | 20.0 | 49.0 | 26.0 | 31.0 | 103.0 |
| | | P2 | 50-90 | 6.8 | 0.2 | 0.009 | 6.8 | 0.2 | 7.0 | 20.0 | 11.0 | 19.0 | 34.0 |
| | | P3 | 90-120 | 6.9 | 0.4 | 0.033 | 11.1 | 0.2 | 15.0 | 45.0 | 22.0 | 24.0 | 72.0 |
| | | P4 | 120-150 | 7.2 | 0.05 | 0.006 | 3.9 | 0.1 | 5.0 | 10.0 | 6.0 | 7.0 | 16.0 |
| **depression** alluvial gley *(Vega-Gley)* of alluvial loam | 22.8[4] | D1 | 10-20 | 6.5 | 7.2 | 0.534 | **124.2** | 12.4 | 283.0 | 206.0 | 70.0 | 305.0 | 1266.0 |
| | | D2 | 20-50 | 6.8 | 1.1 | 0.108 | **62.6** | 1.7 | 45.0 | 77.0 | 38.0 | 100.0 | 317.0 |
| | | D3 | >70 | 6.9 | 0.07 | 0.008 | 2.7 | 0.2 | 7.0 | 8.0 | 5.0 | 6.0 | 21.0 |

*[1] masl= metre above sea level*
*[2] less flooded*
*[3] medium flooded*
*[4] highly flooded*
*[5] H=horizon, In brackets: threshold values according to the BBodSchV 1999 (action value for grassland)*
*Bold: threshold exceedances regarding the BBodSchV 1999)*

Total metal and As concentrations of the soil were quantified after digestion using aqua regia (37% HCl + 65% HNO3, 3:1) ignoring the immobile silica-bound fraction. Basic properties and total TM contents of the studied soils are presented in Table 3.1.

### 3.2.3 Monitoring river water level, soil parameters and dissolved trace metal contents

At each plot we installed field monitoring stations to observe soil parameters and to indicate biogeochemical changes within the soil solution. Due to the high amount of different sensors we could not equip the top soil layer, mainly for maintaining stabilised conditions within the soil profile especially under flood events. We installed sensors at three different depths (levee: L1–L3; depression: D1–D3), resp. four within the plateau (P1–P4); FDR- (Frequency Domain Reflectometry) or TDR- (Time Domain Reflectometry) sensors for measuring volumetric soil moisture content (Feu) and sensors for measuring the redox potential ($E_H$) as well as soil temperature. We used five repetitions for the redox sensors on the levee and the depression and three repetitions on the plateau. For temperature and soil moisture measurements we only used one sensor per horizon. Data were monitored daily every full hour through a data logger. Beyond we installed suction cups for collecting soil solution samples. The suction cups were installed in three repetitions for all plots. Under high water levels (surface and/or groundwater) soil solution samples were taken at all depths at all plots once a week, resp. during floods every day. To extract soil solution, a vacuum of maximal 0.6 bar was applied to the samplers (1-liter bottles) for one week. At the time of sampling the vacuum was first applied to empty all of the tubes and then again to take the samples. The soil solution samples were immediately filtered through a 0.45 µm Millipore membrane (Whatman Inc., USA) into two sub-samples and stored at 4 °C until they were transferred to the laboratory for individual analyses. One sub-sample was used to monitor concentrations of DOC, which was analysed using a TOC-V (Shimadzu, Japan). To the other sub-sample, 3 drops of 2M $HNO_3$ were added to preserve the solution for later analysis. TM concentrations (As, Cd, Cu, Cr, Ni, Zn) in the soil solution were analysed on ICP-MS using an ELAN 5000 (PerkinElmer, Shelton, CT, USA). We further analysed the soil solution for Fe, Mn, $NO_3$-N and sulphate with an ion chromatograph (IC 120, Dionex, USA) as well the pH-value using a WTW probe. Beyond we also collected data on the river water level (WL) at the gauge Wittenberge (BfG, 2005–2008). Data were sampled from July 2005 until August 2008.

### 3.2.4 Data analysis and generalised additive and mixed modelling

To identify spatial patterns along the topographical gradient a canonical correspondence analysis (CCA) was carried out (not shown). The input data were the total TM content as well as altitude, horizon, the C/N ratio and pH-value as environmental variables.

The CCA showed soil parameters and total TM content to differ markedly between the plots, segregating them and affirming the selection of the studied plots. For further data exploration we used multi-panel Cleveland dotplots to visualise the relationship between TMs and the explanatory variables. Here we also identified the existing non available data (NAs). Because the amount of soil solution is strongly dependent on the WL we need to handle significant differences regarding the available data sets per plot (App. A1–A3). Further we used box plots to explore seasonal as well spatial differences between $E_H$, pH-value and soil moisture and between TM release from soils (Figs. 3.3, 3.4). Because seasonality is a measure of dissolved TMs we did not standardise the time series and gave them all equal importance. For nearly all investigated TMs and explanatory variables seasonal as well spatial patterns were identified. The same could also be found in terms of dissolved TM contents within the soil profile. This means that seasonal effects and vertical differences within the soil profile have to be included in further analysis. Thus we applied generalised additive models (GAMs) on TM time series data. These models are smoothing models that allow for non-linear relationships between response and multiple explanatory variables (Zuur et al. 2009), enabling us to identify spatial and seasonal patterns as well name important explanatory variables for TM mobility in floodplain soils. We built distinct models for each TM and for each studied plot. To account for vertical differences within the soil profiles and possible temporal effects we included horizon, day and year as predictors. The full data sample is used for both model fitting and model selection. The predictors were selected using a stepwise model selection criterion, starting from fitting a full GAM in which all explanatory variables were included. The procedure omits the variable with the highest P-value if greater than 0.1 (thus has no significant effect) at each step and evaluates the alternative model by comparing the Akaike's Information Criterion (AIC). If the alternative model has lower AIC than the full model, the variable is to be excluded from further modelling. The model with the lowest AIC was selected and reported. Due to fluctuating soil solution quantities over the year and between the three plots the fitted models per plot are different from each other concerning the available and thus used predictors. The fitted, full starting models we used are given below:

Equation 1:

$$TM_{i(levee)} = \alpha_i + \beta_i + f_i\,(WL) + f_i\,(E_H) + f_i\,(Feu) + f_i\,(Mn) + f_i\,(day)\; + \\ factor\,(horizon) + factor\,(year) + \varepsilon_i$$

Equation 2:

$$TM_{i(ldepression)} = \alpha_i + \beta_i + f_i\,(WL) + f_i\,(E_H) + f_i\,(pH) + f_i\,(Fe) + f_i\,(Mn) + f_i\,(SO_4^{2}) + f_i\,(day)\; + \\ factor\,(horizon) + factor\,(year) + \varepsilon i$$

Equation 3:

$$TM_{i(plateau)} = \alpha_i + \beta_i + f_i\,(WL) + f_i\,(E_H) + f_i\,(Feu) + (day)\; + \\ factor\,(horizon) + factor\,(year) + \varepsilon_i$$

$TM_i$ is the response variable and stands for the several TMs (As, Cd, Cu, Cr, Ni, Zn), α is the intercept, β is the slope, $f(X_i)$ stands for the several explanatory variables. For obtaining general information about existing relations between TM release and $E_H$ and seasonal changes we also fitted a model for all TMs together (App. B1-B2). For a more detailed identification of seasonal and spatial patterns of TM dissolution between and within the plots we carried out generalised additive mixed models (GAMMs). Here we excluded soil parameters and attempted to make time and space more visible by simply including day and horizon as explanatory variables and defined the three plots as random effects. We fitted one model for each TM:

Equation 4:

$$TM_{i(all)} = \alpha_i + \beta_i + f_i\ (day, by{=}horizon), random{=}list(fstation{=}\sim 1)) + \varepsilon_i$$

All statistical analyses were performed with the packages lattice, mgcv, vegan, ade4 in the R environment (version 2.14.2; R Development Core Team 2011).

### 3.2.5 Model validation

The selected models were checked for violation of homogeneity (fitted against residual values), independence (residual values against all covariates), influential observations (cooks distance) and normality (histograms) by graphical outputs. Those plots are diagnostic tools for visualising how well the statistical model fits the data, whether it need to be improved, and to compare the fit of different models. The 'goodness-of-fit' of the selected models was also evaluated by the deviance explained and the total degree of freedom.

## 3.3 Results

### 3.3.1 Sediment sampling

Table 3.1 gives an overview about soil parameters as well as the total TM content for each plot. The depression plot (DP) shows the highest total TM content in the two upper horizons (D1, D2). For As even the threshold values of the German Soil Protection Guideline (BBodSchV, 1999) are exceeded. Soils of this plot also show highest carbon content and almost neutral pH-values for all soil horizons. Within the soil profile of the plateau plot (PP) only P1 and P3 show higher elevated total TM contents; pH-values are also almost neutral, even though the carbon content is rather low. TM amounts within the levee plot (LP) are rather low and comparable between the different horizons. Here, the acidic pH-value is remarkable.

### 3.3.2 Monitoring the river water level, soil parameters and dissolved trace metal contents

Figure 3.2 shows the course of the water level of the river Elbe at the gauge Wittenberge. During the sampling period hydrological conditions within the river varied considerably and showed three very different flood events. We monitored one very high flood in spring 2006, during which all plots within the floodplain were flooded. Furthermore, a much lower and short flood event was recorded in spring 2007 and lastly a very long but also lower flood event was documented from late autumn 2007 until spring 2008.

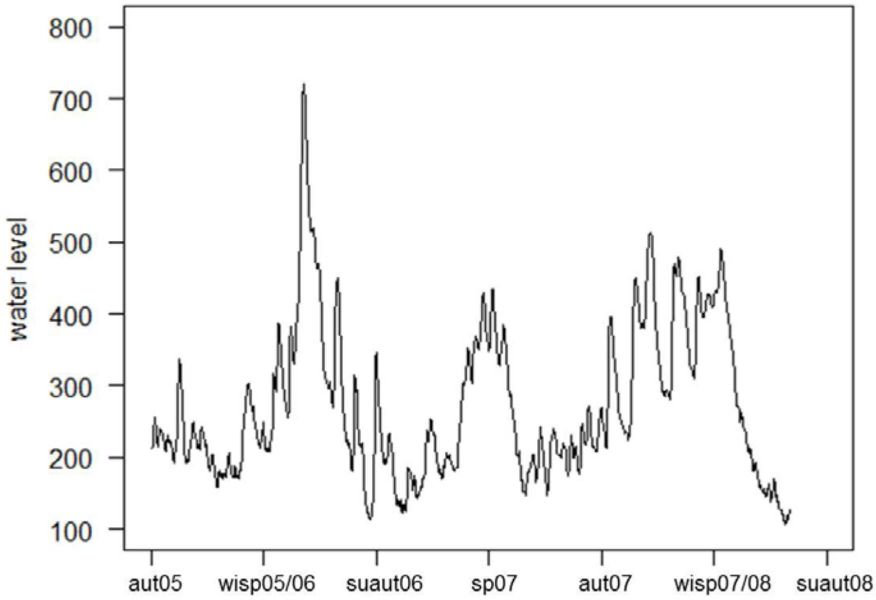



Figure 3.2 Hydrograph of the river Elbe from July 2005 until August 2008 at the gauge Wittenberge (BfG 2005-2008*)*
*(aut=autumn, wisp= winter/spring, suaut= summer autumn, sp=spring)*

During the last two events only the DP was completely flooded by surface water, while the other two plots showed higher groundwater levels. According to these seasonal river water level fluctuations soil parameters ($E_H$, pH-value and Feu) within floodplain soils also changed significantly depending on the different plots and horizons (Fig. 3.3). Paramount variances within the redox potential occur for the DP (D1–D3), especially for D1. For the PP (P1–P4) each soil horizon shows lower extremes, but the lowest median level occurs for P2. As far as the LP (L1–L3) are concerned, redox potential only decrease significantly in L3. Soil moisture remains almost constant in all soil horizons of the LP, while showing high variations in the other two plots. Most obvious are the low pH-value within the LP.

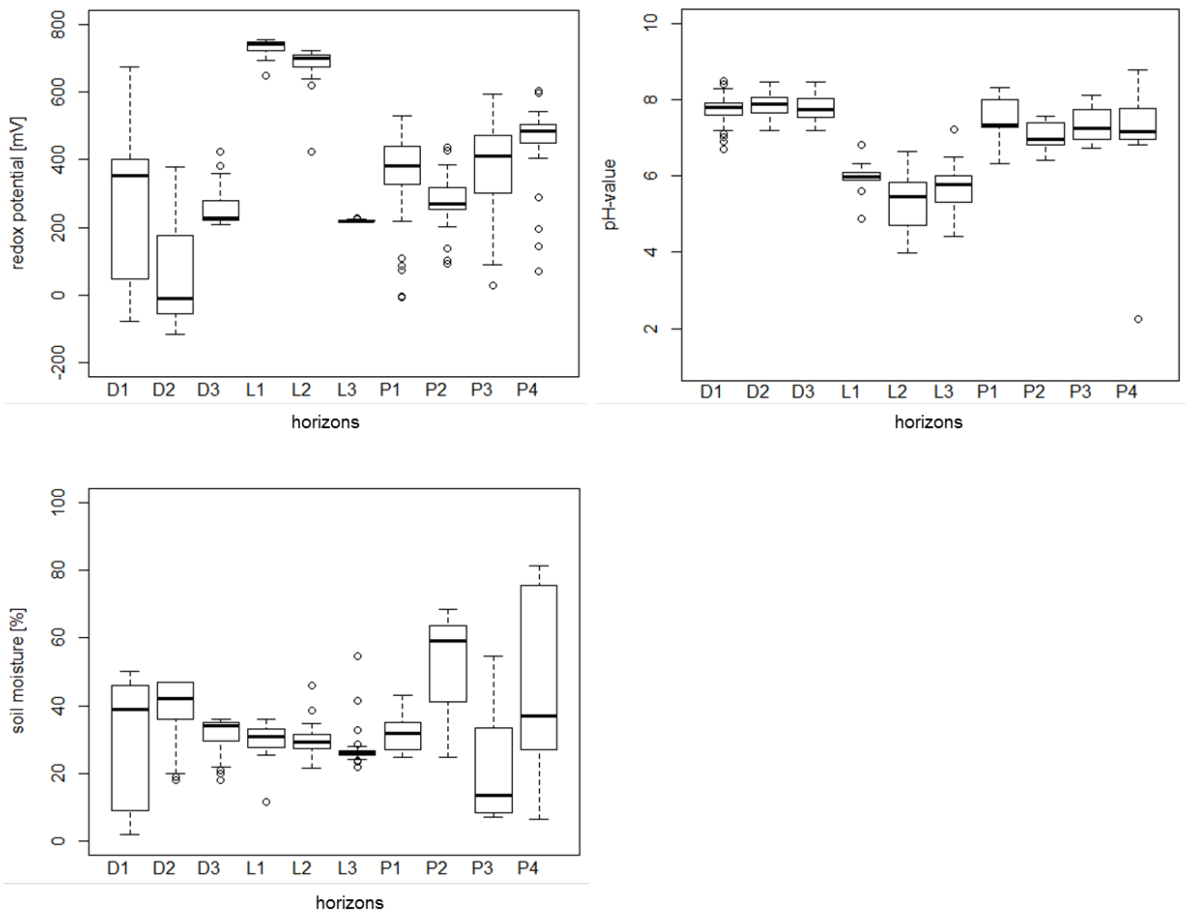



Figure 3.3 Plot- and horizon-specific distribution of $E_H$, pH-value and soil moisture *(D1-D3 = depression horizons, highly flooded; L1-L3 = levee horizons, slightly flooded; P1-P4 = plateau horizons, medium flooded)*

The results obtained from the dissolved TM contents were not expected at all (Fig. 3.4). Highest dissolved median concentrations of Cd, Cr, Ni, Zn were found in the slightly flooded and consequently the plot with the least overall pollution, namely the LP. By contrast, the highest measured maximum values of As, Cu and Cr could be detected in the D3 horizon of the highly flooded and thus highly polluted DP. It was only for As where the highly-flooded plot also showed the highest maximum and median dissolved concentrations for all horizons. For better visibility, here, we included a box plot in which extreme outliers are removed. Compared to these the medium flooded plot, the PP, only displayed medium dissolved TM concentrations.

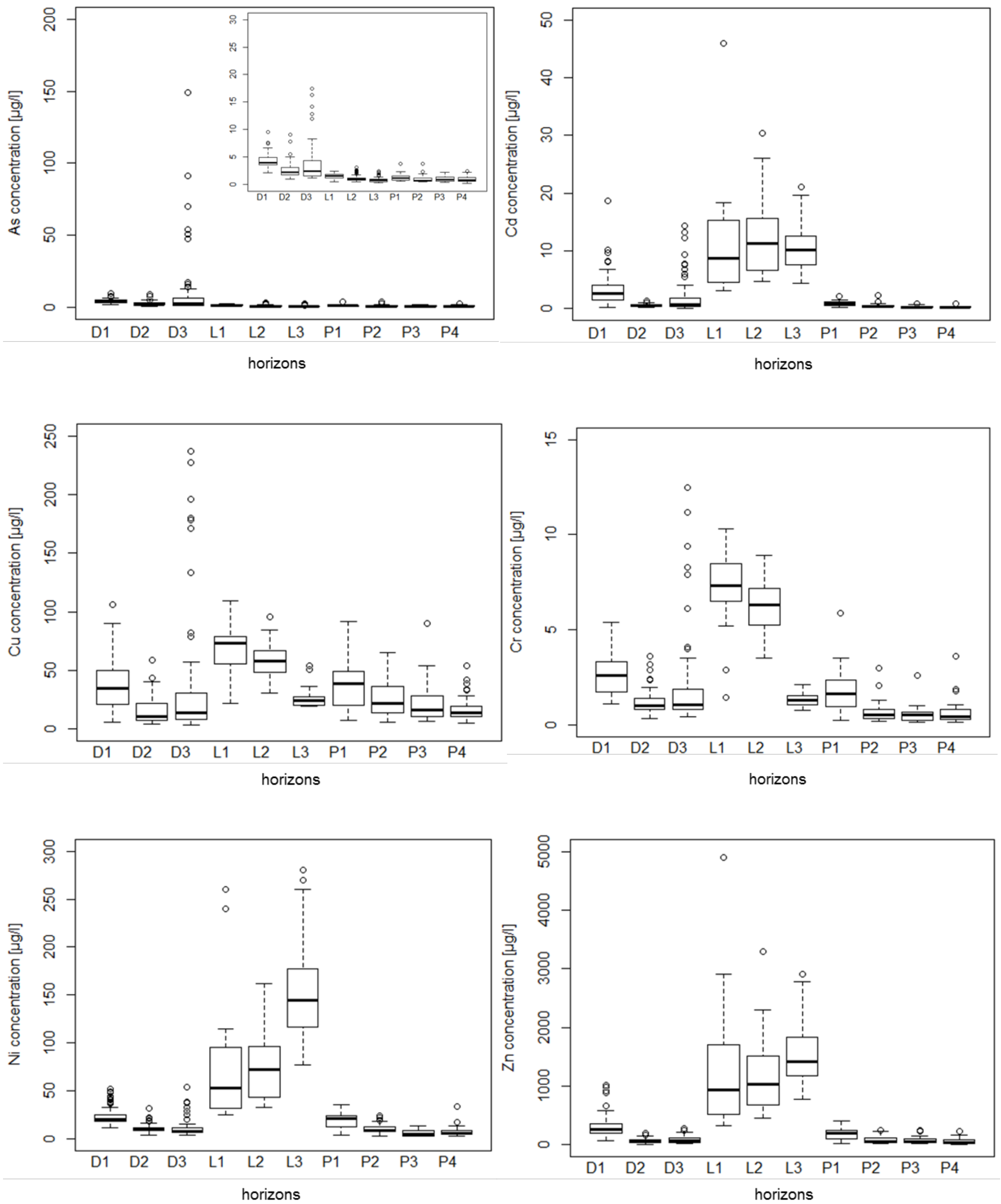



Figure 3.4 Plot- and horizon-specific distributions of TMs
*(D1-D3 = depression horizons, highly flooded, L1-L3 = levee horizons, slightly flooded P1-P4 = plateau horizons, medium flooded)*

### 3.3.3 Explaining the variation of TM release - generalised additive and mixed modelling

GAMs showed a great potential to interpret the relationship between TM release and the monitored biogeochemical characteristics of the three plots. Table 3.2 gives the results of the final GAMs for each TM per plot. The explained deviance of the models ranged from 51.6% to 92.6%. A direct comparison between the models and thus the plots is rather difficult because of differences in the data availability. In general the 'goodness-of-fit' of the models was lowest in the PP and best in the LP. However, model validations suggest that the model fitted the observed data reasonably well even in the PP where no soil solution parameter could be included due to the high amount of NAs within the data set. Within the chosen parameters per plot $E_H$ seem to be highly influential in the LP and DP. Also Feu contributes significantly to TM release within LP and PP (not included in DP). In all models spatial (horizon) and temporal effects (year, day) are important related to TM release from soils. Since those spatial and seasonal factors appear to play a major role in TM mobility for almost all cases, we performed GAMMs combined for all plots but separately for the several TMs.

*Table 3.2 Summary statistics for the best fitted GAMs for TM dissolution during field measurements from 2005 to 2008*
*(D.E.= deviance explained, Total df= total degrees of freedom)*

| predictors | F-value | p-value | Model performance | | |
|---|---|---|---|---|---|
| | | | D.E. | Total df | n |
| **LP** | | | | | |
| **As** | | | 86.4 | 27.51 | 110 |
| fhorizon | 7,24 | **<0,01** | | | |
| fyear | 12,5 | **<0,001** | | | |
| $E_H$ | 0,90 | 0,44 | | | |
| Soil moisture | 1,45 | 0,22 | | | |
| Mn | 3,65 | **<0,001** | | | |
| day | 8,95 | **<0,001** | | | |
| **Cd** | | | 92.6 | 36.55 | 110 |
| fhorizon | 8,60 | **<0.001** | | | |
| fyear | 19,44 | **<0.001** | | | |
| Water level | 0,71 | 0.51 | | | |
| $E_H$ | 3,1 | **<0.01** | | | |
| Soil mositure | 4,0 | **<0.001** | | | |
| Mn | 9,44 | **<0.001** | | | |
| day | 9,40 | **<0.001** | | | |
| **Cu** | | | 92.5 | 29.65 | 110 |
| fhorizon | 3.06 | **<0.1** | | | |
| fyear | 4.64 | **<0.01** | | | |
| Water level | 2.98 | **<0.05** | | | |
| $E_H$ | 2.95 | **<0.01** | | | |
| Soil mositure | 2.46 | 0.12 | | | |
| Mn | 1.87 | **<0.1** | | | |
| day | 6.68 | **<0.001** | | | |
| **Cr** | | | 91.8 | 13.81 | 107 |
| fhorizon | 405.7 | **<0.001** | | | |
| fyear | 1.40 | 0.24 | | | |
| Water level | 5.36 | **<0.05** | | | |
| Soil moisture | 2.60 | **<0.1** | | | |
| day | 8.12 | **<0.001** | | | |
| **Ni** | | | 96.1 | 38.79 | 107 |
| fyear | 15.76 | **<0.001** | | | |
| Water level | 2.12 | **<0.05** | | | |
| $E_H$ | 28.27 | **<0.001** | | | |
| Soil mositure | 2.72 | **<0.05** | | | |
| Mn | 8.55 | **<0.001** | | | |
| day | 9.42 | **<0.001** | | | |
| **Zn** | | | 91.3 | 29.75 | 107 |
| fyear | 5.96 | **<0.01** | | | |
| Water level | 2.56 | **<0.05** | | | |
| $E_H$ | 81.52 | **<0.001** | | | |
| Soil mositure | 3.38 | **<0.01** | | | |
| Mn | 11.23 | **<0,001** | | | |
| day | 7.48 | **<0,001** | | | |
| **DP** | | | | | |
| **As** | | | 78.5 | 24.21 | 97 |
| fhorizon | 32.82 | **<0.001** | | | |
| fyear | 2.70 | **<0.1** | | | |
| $E_H$ | 2.91 | **<0.01** | | | |
| Mn | 2.32 | **<0.05** | | | |
| Fe | 5.44 | **<0.001** | | | |
| **Cd** | | | 88.8 | 31.74 | 91 |
| fhorizon | 44.37 | **<0.001** | | | |
| fyear | 2.37 | **<0.1** | | | |
| Water level | 9.54 | **<0.01** | | | |
| $E_H$ | 4.82 | **<0.001** | | | |
| pH | 3.45 | **<0.1** | | | |
| Fe | 3.71 | **<0.01** | | | |
| Mn | 5.48 | **<0.001** | | | |
| $SO_4^{2}$ | 2.82 | **<0.05** | | | |
| **Cu** | | | 77.3 | 25.18 | 102 |
| fhorizon | 8.22 | **<0.001** | | | |
| fyear | 5.07 | **<0.01** | | | |
| $E_H$ | 8.72 | **<0.001** | | | |
| pH | 8.27 | **<0.05** | | | |
| Mn | 4.59 | **<0.1** | | | |
| **Cr** | | | 86.4 | 30.51 | 102 |
| fhorizon | 24.59 | **<0.001** | | | |
| fyear | 4.60 | **<0.01** | | | |
| Water level | 2.49 | **<0.05** | | | |
| $E_H$ | 4.43 | **<0.001** | | | |
| Fe | 11.35 | **<0.001** | | | |
| Mn | 1.31 | 0.26 | | | |
| $SO_4^{2}$ | 1.66 | 0.14 | | | |
| day | 2.84 | **<0.1** | | | |

| predictors | F-value | p-value | Model performance | | |
|---|---|---|---|---|---|
| | | | D.E. | Total df | n |
| **Ni** | | | 89.3 | 17.47 | 102 |
| fhorizon | 80.79 | **<0.001** | | | |
| $E_H$ | 2.53 | **<0.05** | | | |
| pH | 3.08 | **<0.1** | | | |
| Fe | 7.21 | **<0.001** | | | |
| Mn | 15.33 | **<0.001** | | | |
| $SO_4^{2}$ | 4.28 | **<0.01** | | | |
| day | 2.76 | 0.10 | | | |
| **Zn** | | | 89.6 | 20.70 | 102 |
| fhorizon | 111.0 | **<0.001** | | | |
| fyear | 1.68 | 0.18 | | | |
| Water level | 12.00 | **<0.001** | | | |
| $E_H$ | 3.821 | **<0.01** | | | |
| Mn | 1.37 | 0.24 | | | |
| $SO_4^{2}$ | 2.06 | **<0.1** | | | |
| day | 3.13 | **<0.05** | | | |
| **PP** | | | | | |
| **As** | | | 78.5 | 24.21 | 97 |
| fhorizon | 6.84 | **<0.001** | | | |
| fyear | 9.39 | **<0.001** | | | |
| $E_H$ | 3.23 | **<0.1** | | | |
| Soil Moisture | 2.64 | 0.11 | | | |
| day | 10.90 | **<0.001** | | | |
| **Cd** | | | 69.4 | 14.43 | 114 |
| fhorizon | 36.0 | **<0.001** | | | |
| fyear | 4.96 | **<0.01** | | | |
| Water level | 4.20 | **<0.05** | | | |
| Soil Moisture | 1.98 | 0.13 | | | |
| day | 2.21 | **<0.1** | | | |
| **Cu** | | | 51.6 | 13.43 | 115 |
| fhorizon | 10.43 | **<0.001** | | | |
| fyear | 10.01 | **<0.001** | | | |
| Water level | 2.51 | **<0.1** | | | |
| Soil Moisture | 1.35 | 0.26 | | | |
| day | 7.14 | **<0.01** | | | |
| **Cr** | | | 59.4 | 16.73 | 102 |
| fhorizon | 6.11 | **<0.001** | | | |
| fyear | 7.28 | **<0.001** | | | |
| Soil Moisture | 2.43 | **<0.05** | | | |
| day | 1.42 | 0.24 | | | |
| **Ni** | | | 72.8 | 21.08 | 115 |
| fhorizon | 24.19 | **<0.001** | | | |
| fyear | 2.27 | **<0.1** | | | |
| Water level | 4.65 | **<0.05** | | | |
| $E_H$ | 1.18 | 0.31 | | | |
| Soil Moisture | 2.71 | **<0.05** | | | |
| day | 2.00 | **<0.1** | | | |
| **Zn** | | | 63.9 | 16.02 | 115 |
| fhorizon | **15.32** | **<0.001** | | | |
| fyear | **16.73** | **<0.001** | | | |
| $E_H$ | **2.42** | 0.13 | | | |
| Soil Moisture | **3.13** | **<0.1** | | | |
| day | **4.16** | **<0.001** | | | |

Overall the released TM amounts from the LP (L1–L3) show a significant horizon as well a seasonal-specific pattern. Here the results from the data exploration could be confirmed since for all investigated TMs (except for As) this plot could be identified as a hot spot for dissolved TMs. Beyond, hot moments in terms of TM release were recognised for Cu, Cr, Ni and Zn in L3. It is shown that the hot moment is around the same time for all of these metals, reaching maximum dissolution rates around day 250 which is in late summer. For the DP hot spots are also identified for all investigated TMs, but only for As also a hot moment in D3 appears around day 100 that represents early spring (Fig. 3.5). For PP no hot moments could be observed, although for Cu and Cr this plot is also a hot spot for dissolved TMs.

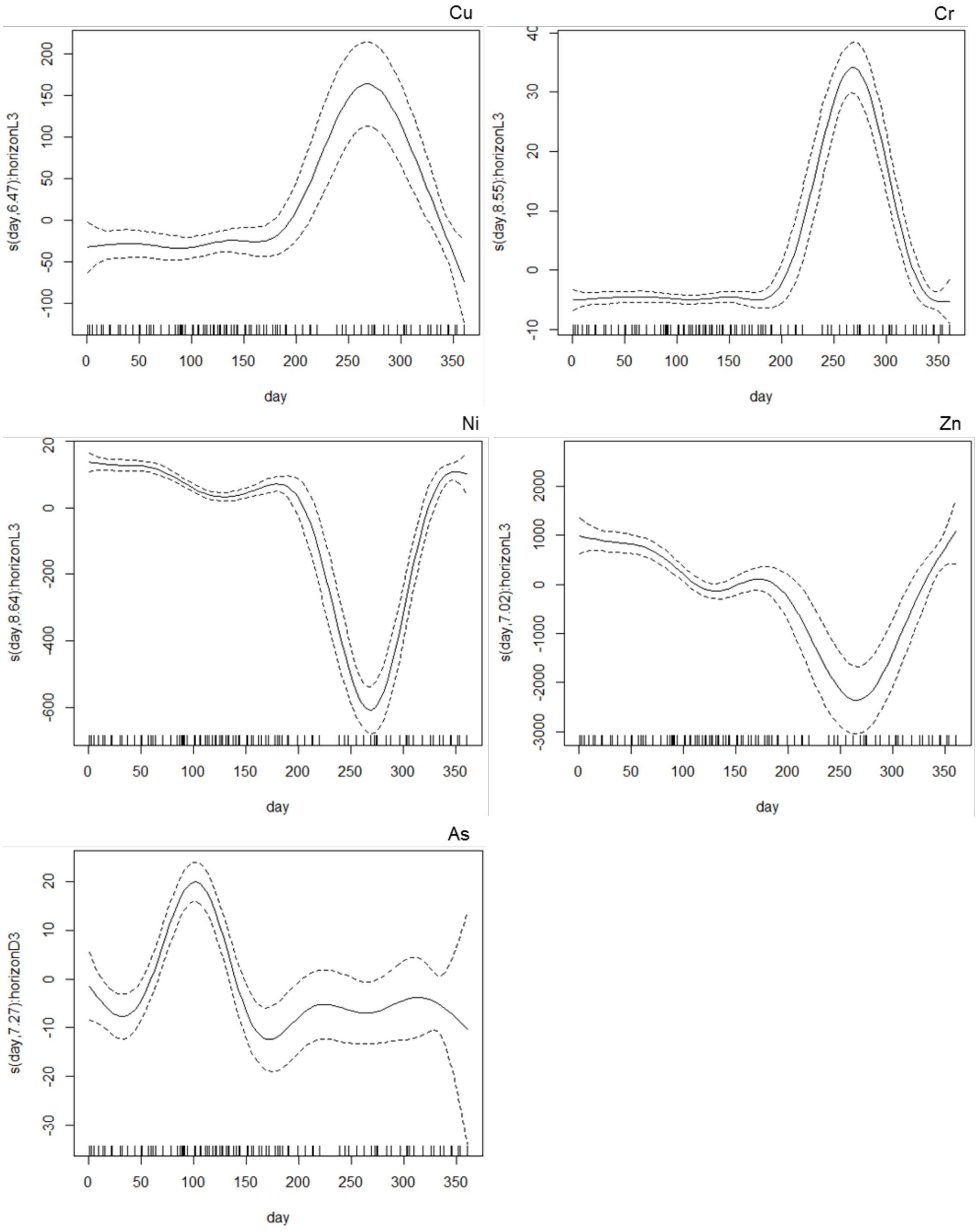



Figure 3.5 Smoothers and 95% point wise confidence bands from the GAMMs.
*Hot moments could be identified for Cu, L3 (P<0.001, F=8.91); Cr, L3 (P<0.001, F=55.06); Ni, L3 (P<0.001, F=72.06); and Zn, L3 (P<0.001, F=21.43, As, D3 (P<0.001, F=14.44). Estimated degrees of freedom are given in the y-axis label.*

## 3.4 Discussion

The most obvious and dynamic connections in riverine landscapes are those between the main channel of a river or stream and the floodplain (Amoros and Roux 1988). Here, connectivity is a seasonal phenomenon, driven by the occasion and the extent of floods, determining the importance of altering the seasonally-pulsed connectivity between aquatic and terrestrial ecosystems (Wiens 2002). At the time of flooding soil parameters such as $E_H$ and soil moisture and related factors like pH-value and compounds such as iron and manganese oxides change significantly (Schulz-Zunkel and Krueger 2009), resulting in changes in the amount of dissolved and thus mobile TMs. During wet periods, elevated dissolved amounts of TMs were expected and also found in the soil solution of all plots. Taking into account the soil-groundwater pathway of the German Soil Protection Guidelines (BBodSchV 1999), soil water concentrations should not exceed 10 µg/l for As, 5 µg/l for Cd, 50 µg/l for Cu, 50 µg/l for Cr, 50 µg/l for Ni and 500 µg/l for Zn. In particular, the DP with a high frequency of flooding, the highest total TM content as well as the highest organic matter content were assumed to be a transformation hot spot because of prevalent anoxic conditions and the presence of electron acceptors (McClain et al. 2003) and thus highest dissolved TM concentrations were expected. However, the most elevated levels were found on the LP, the least overall polluted plot. Dissolved TM concentrations seasonally ranged between Cd: 3.1– 46 µg/l, Cu: 19.1–109 µg/l, Cr: 0.7–10.3 µg/l, Ni: 25–280 µg/l, Zn: 330–4900 µg/l and nearly all of them meet the given threshold values. Contrary, only outliers of the dissolved TM contents of the DP meet the threshold values (Cd: 18.6 µg/l, Cu: 237 µg/l, Ni: 54.4 µg/l, Zn: 1011 µg/l) but here transgressions were almost 5 times higher than those values. Amounts of dissolved TMs within the PP, the medium polluted plot, are only slightly elevated for Cu (4.8–92 µg/l). Elevated concentrations of As could only be found in the soil solution of the DP. Here we found ranges from 0.94 to 149 µg/l. Concentrations of As for the other plots were well below threshold values (LP: 0.32–3.1 µg/l, PP: 0.22–3.8 µg/l). In general these results are in line with the findings from Schulz-Zunkel and Krueger (2009) who presented a mobility row for river Elbe alluvial soils, showing the percentage of the mobile compared to the total amount of TMs: Cd(3.6%) >> Zn(0.9%) > Cu(0.2%) >> As(0.07%) > Pb (0.03%) (n=16), under field conditions. But this only appears to be applicable to continuously moist soils due to the fact that soils which have dried out and remoistened behave differently (Bartlett and James 1979). Therefore, the increased levels of TMs in the soil solution could mostly be explained by the higher solubility of organic matter combined with higher microbial effects and possibly also pH-value effects triggered by the wetting of formerly dried soils (Tack et al. 2006). Beyond that, the highest total contents of TMs were often found in soils that also showed the highest amounts of organic matter as well as clay content with a very high buffer capacity (300 mmoleq/kg and greater) thus preventing TM remobilisation (Rupp et al. 2000). In this study we found seasonally-driven biogeochemical hot spots within the highest polluted DP but also within the less polluted LP. The former were rather short but very profound because of very high extremes. Furthermore, partially higher TM amounts with increasing soil depth suggest a TM translocation from the upper to the lower horizons within the soil profiles, also leading to the assumption of existing transport hot spots. However, it is well known that TM dissolution is affected by a number of soil properties including pH-value, $E_H$, organic matter, the type and amount of clay minerals, iron, manganese- and aluminium oxides (Schulz-Zunkel and Krueger 2009). Identifying such soil properties under field conditions and being able to relate them to changes in TM dissolution is however much more complicated than under laboratory conditions (Van Griethuysen et al. 2005). Here we tried to explain TM dissolution by changes in soil parameters that are rather easy to measure such as $E_H$ and soil moisture as well as the river water level. However, due to rather weak results of the used GAMs we needed to include further available parameters within the soil solution aware of the problem of limitations in the amount of soil solution samples. Appendix (A1–A3) shows the relations between the several TMs and the sampled explanatory variables. It is shown that several of them might influence TM dissolution, but due to high amounts of NAs we could not use all of those parameters. Though, the results of the GAM indicated that $E_H$ might serve as a predictor for TM dissolution in floodplain soils at least for the DP and LP. Beyond the explaining power of iron and manganese in the DP and LP models show the close relation between $E_H$ and those geochemical processes related. Within the PP soil moisture appeared as one of the most important parameter. Nevertheless, our findings still support recent discussions using the predictive potential of $E_H$ to describe the fate of dissolved TMs in floodplains (Hunting and Van der Geest, 2011). When combining all three plots into one model, results showed seasonal changes in TM dissolution with the course of the $E_H$, leading to a distinction of the investigated TMs according to their $E_H$ and seasonal pattern (App. B1–B2). For As, which is known to be highly redox sensitive (Voegelin et al. 2007), no clear redox pattern could be made out from the data collected. However the seasonal pattern for As were very apparent showing that we can expect to find elevated As concentrations during every measured flood event (early and late spring as well as in winter). For Cd the model clearly projects reduced solubility under anaerobic conditions (Schulz-Zunkel and Krueger 2009) and in our study this usually occurs during the spring floods. In terms of Cu and Cr our results extended beyond the findings of Grybos et al. (2007) since an increase in dissolved amounts during periods with high redox potentials has to be expected. The lowest concentrations of both could be found during periods that are expected to have prolonged high water levels within the soil profile that usually occur in autumn and winter and lead to the assumption that in terms of seasonality and the retention of Cu and Cr autumn/winter floods are more influential. Dissolved amounts of Ni and Zn also display a similar behaviour over the year. High redox potentials lead to lower dissolved amounts and over the year spring floods seem to be of greater importance regarding Ni and Zn solubility, which appear to be time-lagged after flood events. It is therefore evident that for all TMs the redox potential is highly significant for their fate. We can therefore state that changes in soil biogeochemistry triggered by changing water levels within the floodplain are essential for TM dissolution but knowledge about river water level alone is not sufficient to make assumptions about TM behaviour in floodplain soils. However, since $E_H$ is highly connected to the river water level, this clearly reflects seasonal heterogeneity within floodplains and even more profoundly the relation of $E_H$ and season, including soil temperature. Against the background that besides nutrients there are a whole range of other elements including TMs that are important for the effects of biogeochemical and transport hot spots as well hot moments (Vidon et al. 2010), we provided and attempted to interpret data regarding TM dissolution identifying biogeochemical hot spots and hot moments at the scale of the soil profile (McClain et al. 2003). At this scale hot spots occurred at different locations (see McClain et al. 2003) and therefore we can also assume that the hot spots here occur at the anaerobic centre of large soil aggregates and that the reactants are transported into these hot spots by percolating soil water. In unsaturated zones, flow paths are irregular with strong seasonal variations and thus retention or remobilisation hot spots within unsaturated soil profiles will be active during hot moments (McClain et al. 2003). In floodplains such hot moments are usually inundation events. Within the LP that we could identify as a hot spot for dissolved TMs we also found significant hot moments leading to small-scale hot spots solely in L3 and time-lagged after flood events. For Cu and Cr we identified a time-lagged hot spot during late summer and early autumn which confirm the above results that these two metals are remobilised during periods of high redox potentials within the soil but probably only if the water table fluctuates within the soil. Vice-versa this will also apply to Ni and Zn. Hot spots are also shown to be time-lagged after usual flood events but here we found minimum dissolved concentrations of these TMs which confirm that Ni and Zn concentrations decrease with increasing redox potentials in soils. The drying and re-wetting of soils is also assumed to play an important role here, since we measured these effects after wet conditions. We can further assume that the LP soil profile is indeed a transportation hot spot. Within the DP we were able to identify one strong hot spot of increased amounts of dissolved As in the D3 horizon that also coincided with a hot moment which is in this case during a typical flood event in spring. These effects are also located within the deepest assessed horizon, leading to the assumption that the DP is also a transport hot spot. The PP did not show any definable hot moments and thus no significant measurable effects of flood events on TM dissolution at least at this scale.

## 3.5. Conclusion

Floodplain soils are known as net sinks for pollutants including TMs but under certain circumstances such as long-term climate change, they may also act as sources for pollutants. It could be shown that even during ordinary flood events, high amounts of several TMs were dissolved, also at areas that do not show noticeable total TM concentrations. Furthermore, it was found that under field conditions $E_H$ plays an important role in terms of TM release in floodplain soils.

Set these results, the possibility of TM transport via percolating water during periods of flooding should be given serious consideration since the ecotoxicology threat of dissolved TMs in floodplain soils is of undisputed risk as shown even for plots that are not considered to be highly polluted at first sight. Thus the fate of TMs in floodplains needs to be taken under serious consideration in an ecosystem that provides an unusual range of ecosystem functions and services.

Acknowledgements

This paper has been written with data collected during the EU-project Eurolimpacs (EU Contract no. GOCE-CT-2003-505540). We strongly appreciate the very helpful comments from our colleagues from the Department of Conservation Biology at the Helmholtz Centre for Environmental Research (UFZ) during the completion of this work. Furthermore, we thank Sarah Gwillym-Margianto for proofreading the manuscript. Beyond we want to thank the reviewers and the editor for their very helpful comments.

## References

Adams, M.S., Ballin, U., Gaumert, T., Hale, B.W., Kausch, H., Kruse, R., 2001. Monitoring selected indicators of ecological change in the Elbe River since the fall of the Iron Curtain. Environmental Conservation 28:333–344.

Amoros, C., Roux, A.L., 1988. Interaction between water bodies within the floodplains of large rivers: function and development of connectivity. Münstersche Geographische Arbeiten 29:125–130.

ARGE-Elbe (Arbeitsgemeinschaft zur Reinhaltung der Elbe), 1984–2000. Tables of monitoring measurements, Hamburg. *Available at www.arge-elbe.de/wge/Download/DDaten.php (verified 23 Mar. 2009).*

Bartlett, R., James, B., 1979. Behavior of chromium in soils: III. Oxidation. Journal of Environmental Quality 8:31–36.

BBodSchV, 1999. BGBl. I S. 1554, Stand: Geändert durch Art. 2 V v. 23.12.2004 I 3758.

BfG, 2005–2008. Water level data 2005–2008, provided by Federal Institute of Hydrology (BfG), recorded by the Administration of Water and Shipping (WSV).

Ciszewski, D., Czajka, A., Blazej, S., 2008. Rapid migration of heavy metals and (137)Cs in alluvial sediments, Upper Odra River valley, Poland. Environmental Geology 55:1577–1586.

Dong, D.M., Yang, F., Yu, L., Hua, X.Y., Lu, X.J., Zhang, J.J., 2005. Adsorption of Pb, Cd to Fe, Mn oxides in natural freshwater surface coatings developed in different seasons. Journal of Environmental Sciences (China) 17:30–36.

EEA, 1995. Europe's environment. The Dobris assessment, Copenhagen.

Eisenmann, V., 2002. Die Bedeutung der Böden für das Renaturierungspotential von Rückdeichungsgebieten an der Mittleren Elbe. Hamburger Bodenkundliche Arbeiten, 51, PhD.

Graf, M., Lair, G.J., Zehetner, F., Gerzabek, M.H., 2007. Geochemical fractions of copper in soil chronosequences of selected European floodplains. Environmental Pollution 148:788–796.

Grybos, M., Davranche, M., Gruau, G., Petitjean, P., 2007. Is trace metal release in wetland soils controlled by organic matter mobility or Fe-oxyhydroxides reduction? Journal of Colloid and Interface Science 314:490–501.

Hobbelen, P.H.F., Koolhaas, J.E., Van Gestel, C.A.M., 2004. Risk assessment of heavy metal pollution for detritivores in floodplain soils in the Biesbosch, The Netherlands, taking bioavailability into account. Environmental Pollution 129:409–419.

Hunting, E.R., Van der Geest, H.G., 2011. Predictability of bacterial activity and denitrification in aquatic sediments with continuous measurements of redox potential. International Journal of Environmental Science and Technology 8:553–560.

Junk, W.J., Wantzen, K.M., 2004. The Flood Pulse Concept: New Aspects, Approaches, and Applications – an Update, Proceedings of the Second International Symposium on the Management of Large Rivers for Fisheries. RAP Publication. Food and Agriculture Organization and Mekong River Commission, FAO Regional Office for Asia and the Pacific, Bangkok, pp. 117–149.

Krueger, F., Groengroeft, A., 2004. The difficult assessment of heavy metal contamination of soils and plants in Elbe river floodplains. Acta Hydrochimica et Hydrobiologica 31:436–443.

Lair, G.J., Graf, M., Zehetner, F., Gerzabek, M.H., 2008. Distribution of cadmiumamong geochemical fractions in floodplain soils of progressing development. Environmental Pollution 156:207–214.

Masscheleyn, P.H., Pardue, J.H., Delaune, R.D., Patrick, W.H., 1992. Chromiumredox chemistry in a lower Mississippi valley bottomland hardwood wetland. Environmental Science and Technology 26:1217–1226.

McClain, M.E., Boyer, E.W., Dent, C.L., Gergel, S.E., Grimm, N.B., Groffman, P.M., Hart, S.C., Harvey, J.W., Johnston, C.A., Mayorga, E., McDowell, W.H., Pinay, G., 2003. Biogeochemical hot spots and hot moments at the interface of terrestrial and aquatic ecosystems. Ecosystems 6:301–312.

Meybeck, M., Lestel, L., Bonte, P., Moilleron, R., Colin, J.L., Rousselot, O., Herve, D., de Ponteves, C., Grosbois, C., Thevenot, D.R., 2007. Historical perspective of heavymetals contamination (Cd, Cr, Cu, Hg, Pb, Zn) in the Seine River basin (France) following a DPSIR approach (1950–2005). Science of the Total Environment 375:204–231.

Middelkoop, H., 2000. Heavy-metal pollution of the river Rhine and Meuse floodplains in the Netherlands. Geologie En Mijnbouw/Netherlands Journal Of Geosciences 79:411–427.

Mueller, H.W., Schwaighofer, B., Kalman, W., 1994. Heavy-metal contents in river sediments. Water Air and Soil Pollution 72:191–203.

Negrel, P., 1997. Multi-element chemistry of Loire estuary sediments: anthropogenic vs. natural sources. Estuarine Coastal and Shelf Science 44:395–410.

Poot, A., Gillissen, F., Koelmans, A.A., 2007. Effects of flow regime and flooding on heavy metal availability in sediment and soil of a dynamic river system. Environmental Pollution 148:779–787.

Qu, W.C., Kelderman, P., 2001. Heavy metal contents in the Delft canal sediments and suspended solids of the River Rhine: multivariate analysis for source tracing. Chemosphere 45:919–925.

R Development Core Team, 2011. R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria3-900051-07-0 *(URL http:// www.R-project.org/).*

Rupp, H., Krüger, F., Büttner, O., Kunert, M., Meissner, R., Muhs, K., Witter, B., 2000. Wirkung von Hochwasserereignissen auf die Schadstoffbelastung von Auen und kulturwirtschaftlich genutzten Böden im Überschwemmungsbereich von Oka und Elbe. BMBF-Abschlussbericht (FKZ: 02 WT9617/0 209).

Schlichting, E., Blume, H.-P., Stahr, K., 1995. Bodenkundliches Praktikum. Blackwell, Berlin.

Scholten, M., Anlauf, A., Buechele, B., Faulhaber, P., Henle, K., Kofalk, S., Leyer, I., Meyerhoff, J., Purps, J., Rast, G., Scholz, M., 2005. The Elbe River in Germany—present state, conflicting goals, and perspectives of rehabilitation. Large Rivers 15:579–602.

Schulz-Zunkel, C., Krueger, F., 2009. Trace metal dynamics in floodplain soils of the River Elbe: a review. Journal of Environmental Quality 38:1349–1362.

Schwartz, R., 2001. Die Böden der Elbaue bei Lenzen und ihre möglichen Veränderungen nach Rückdeichung. Hamburger Bodenkundliche Arbeiten. 48, Ph.D.

Soares, H., Boaventura, R.A.R., Machado, A., da Silva, J., 1999. Sediments as monitors of heavy metal contamination in the Ave river basin (Portugal): multivariate analysis of data. Environmental Pollution 105:311–323.

Tack, F.M.G., Van Ranst, E., Lievens, C., Vandenberghe, R.E., 2006. Soil solution Cd, Cu and Zn concentrations as affected by short-time drying orwetting: the role of hydrous oxides of Fe and Mn. Geoderma 137:1–2), 83.

Thorp, J.H., Thoms, M.C., Delong, M.D., 2006. The riverine ecosystem synthesis: biocomplexity in river networks across space and time. River Research and Applications 22:123–147.

Tockner, K., Malard, F., Ward, J.V., 2000. An extension of the flood pulse concept. Hydrological Processes 14:2861–2883.

Tockner, K., Lorang, M.S., Stanford, J.A., 2010. River floodplains aremodel ecosystems to test general hydrogeomorphic and ecological concepts. River Research And Applications 26:76–86.

Turner, J.N., Brewer, P.A., Macklin, M.G., 2008. Fluvial-controlled metal and As mobilisation, dispersal and storage in the Rio Guadiamar, SW Spain and its implications for long-term contaminant fluxes to the Donana wetlands. Science of the Total Environment 394:144–161.

Van Griethuysen, C., Luitwieler, M., Joziasse, J., Koelmans, A.A., 2005. Temporal variation of trace metal geochemistry in floodplain lake sediment subject to dynamic hydrological conditions. Environmental Pollution 137:281–294.

Vidon, P., Allan, C., Burns, D., Duval, T.P., Gurwick, N., Inamdar, S., Lowrance, R., Okay, J., Scott, D., Sebestyen, S., 2010. Hot spots and hot moments in riparian zones: potential for improved water quality management. Journal of the American Water Resources Association 46:278–298.

Voegelin, A., Weber, F.A., Kretzschmar, R., 2007. Distribution and speciation of arsenic around roots in a contaminated riparian floodplain soil: micro-XRF elementmapping and EXAFS spectroscopy. Geochimica et Cosmochimica Acta 71:5804–5820.

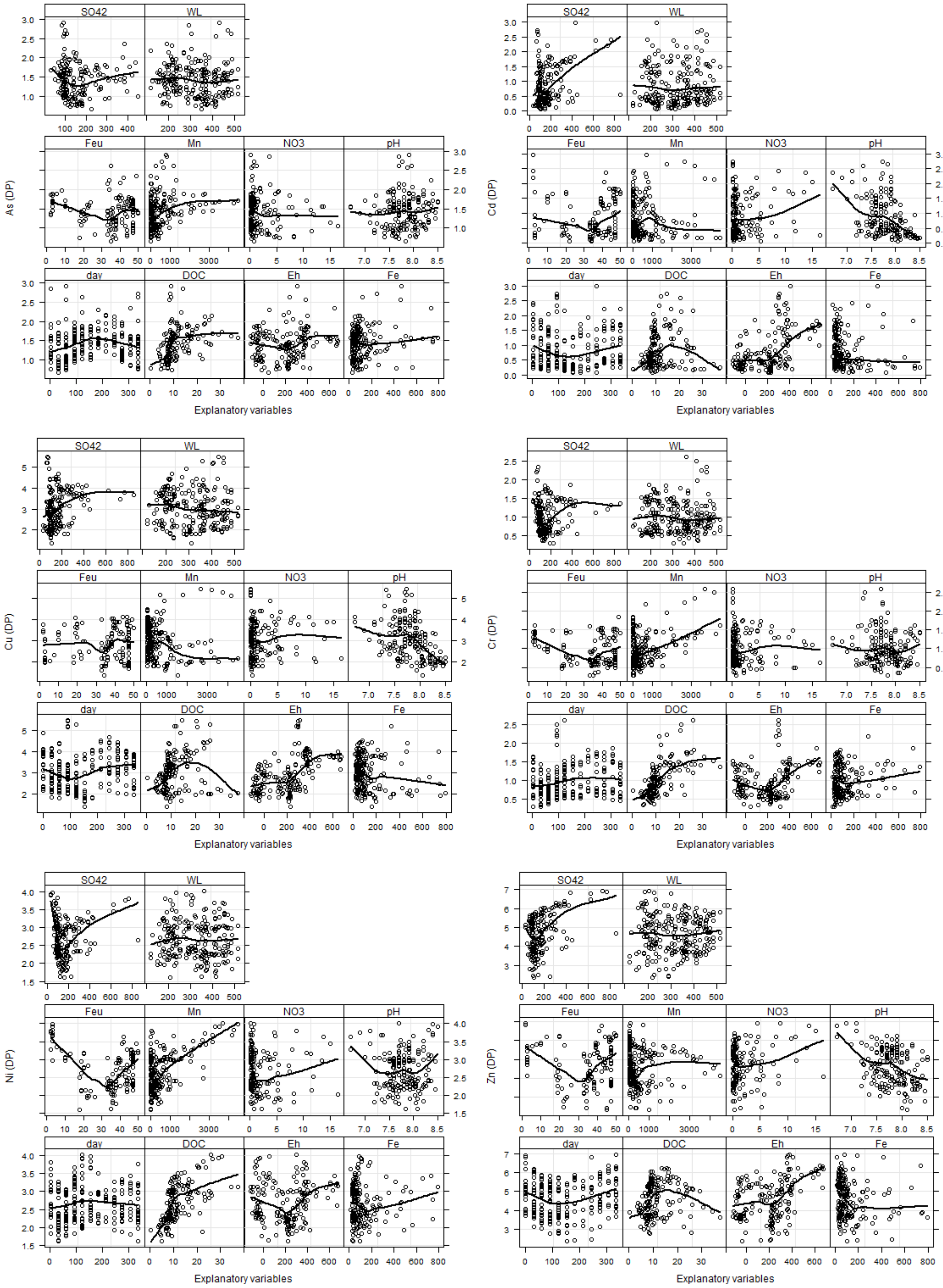
Wiens, J.A., 2002. Riverine landscapes: taking landscape ecology into the water. Freshwater Biology 47:501–515.

Zerling, L., Hanisch, C., Junge, F.W., 2006. Heavy metal inflow into the floodplains at the mouth of the river Weisse Elster (Central Germany). Acta Hydrochimica et Hydrobiologica 34:234–244.

Zuur, A., Ieno, E., Walker, N., Saveliev, A., Smith, G., 2009. Mixed Effects Models and Extensions in Ecology with R. Statistics for Biology and Health. Springer, New York.

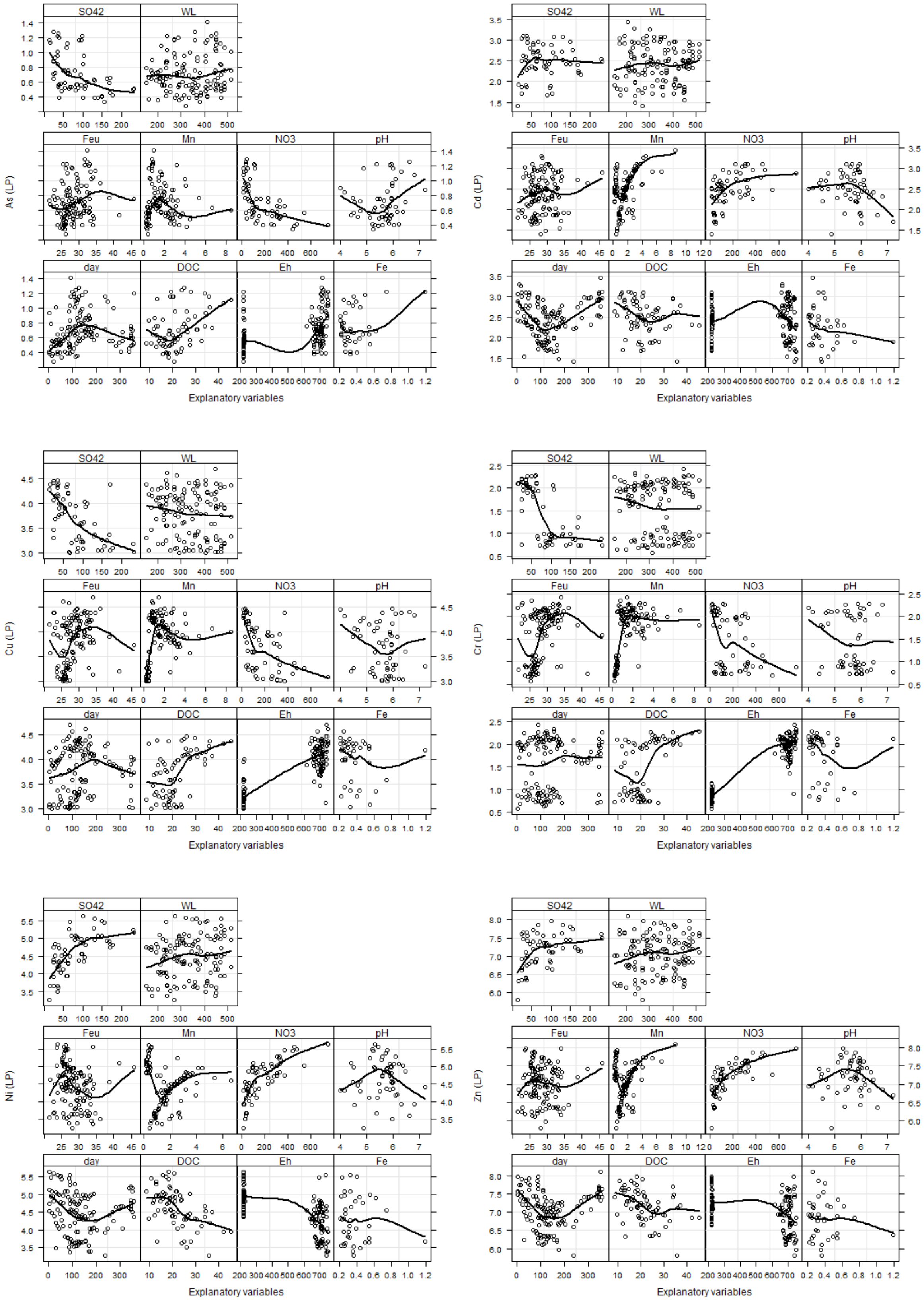
# Appendix A1

Explanatory variables depression plot (DP), *(NA's: Feu: 99, DOC: 75, $NO_3$-N: 61)*



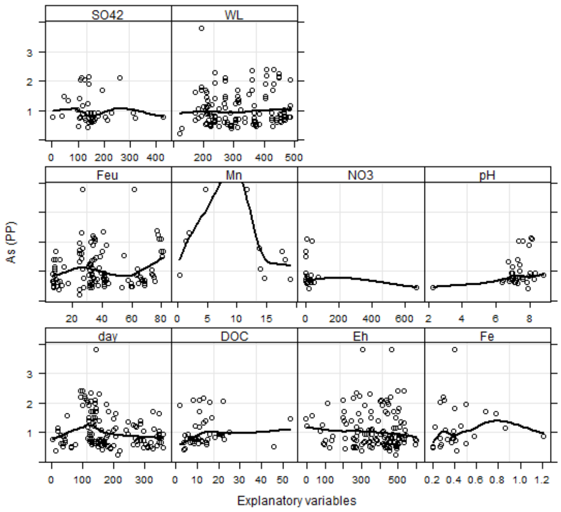
## Appendix A2

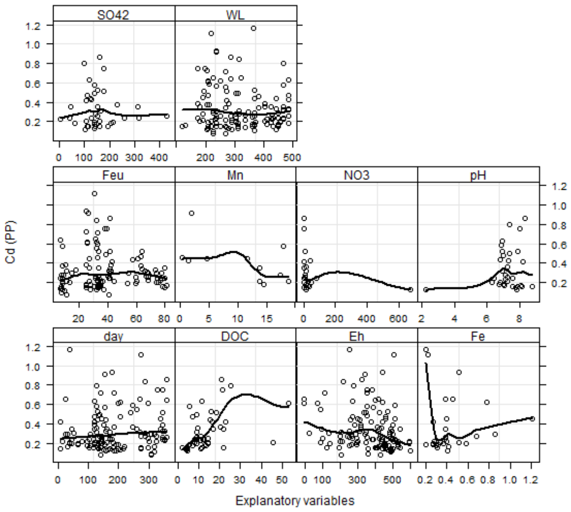
Explanatory variables levee plot (LP), *(NA's: DOC: 66, pH: 79, Fe: 97, $SO_4^{2-}$: 73, $NO_3$-N: 61)*

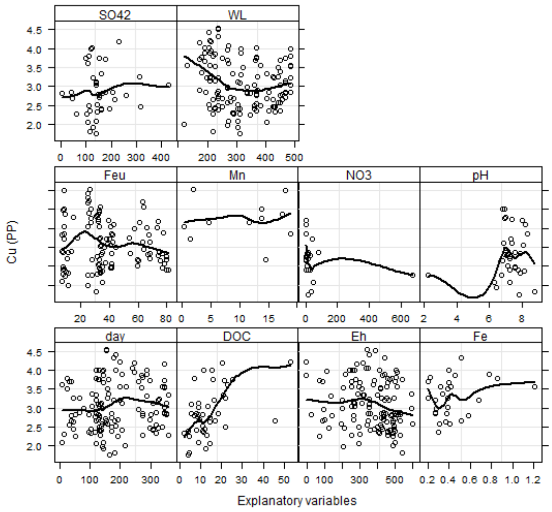


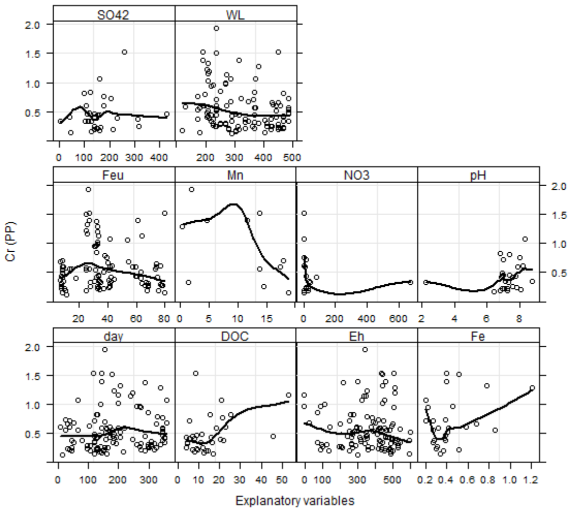
## Appendix A3

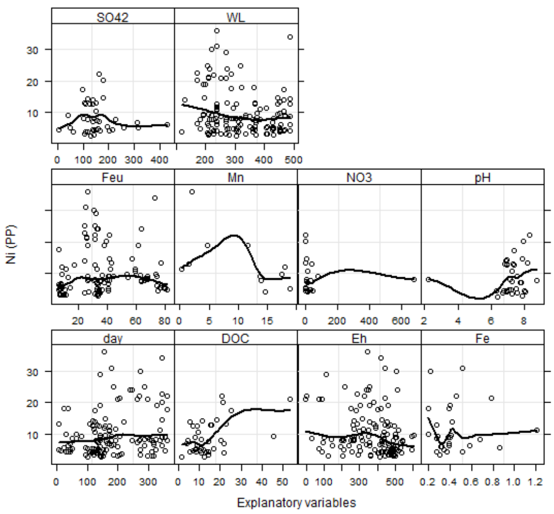
Explanatory variables plateau plot (PP), *(NA's: DOC: 92, pH: 100, Fe: 107, Mn: 124, $SO_4^{2-}$: 94, $NO_3$-N: 113)*

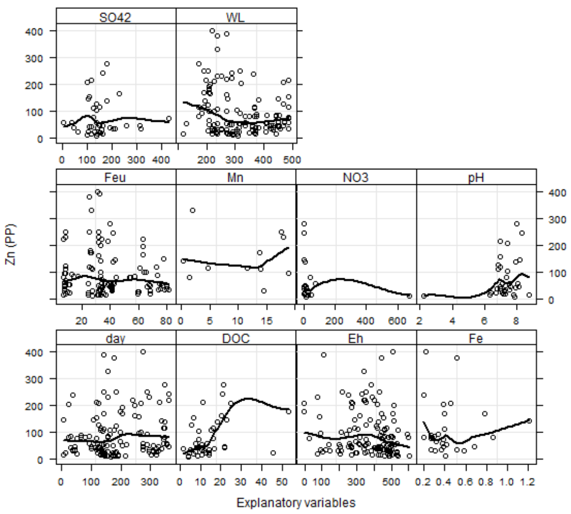


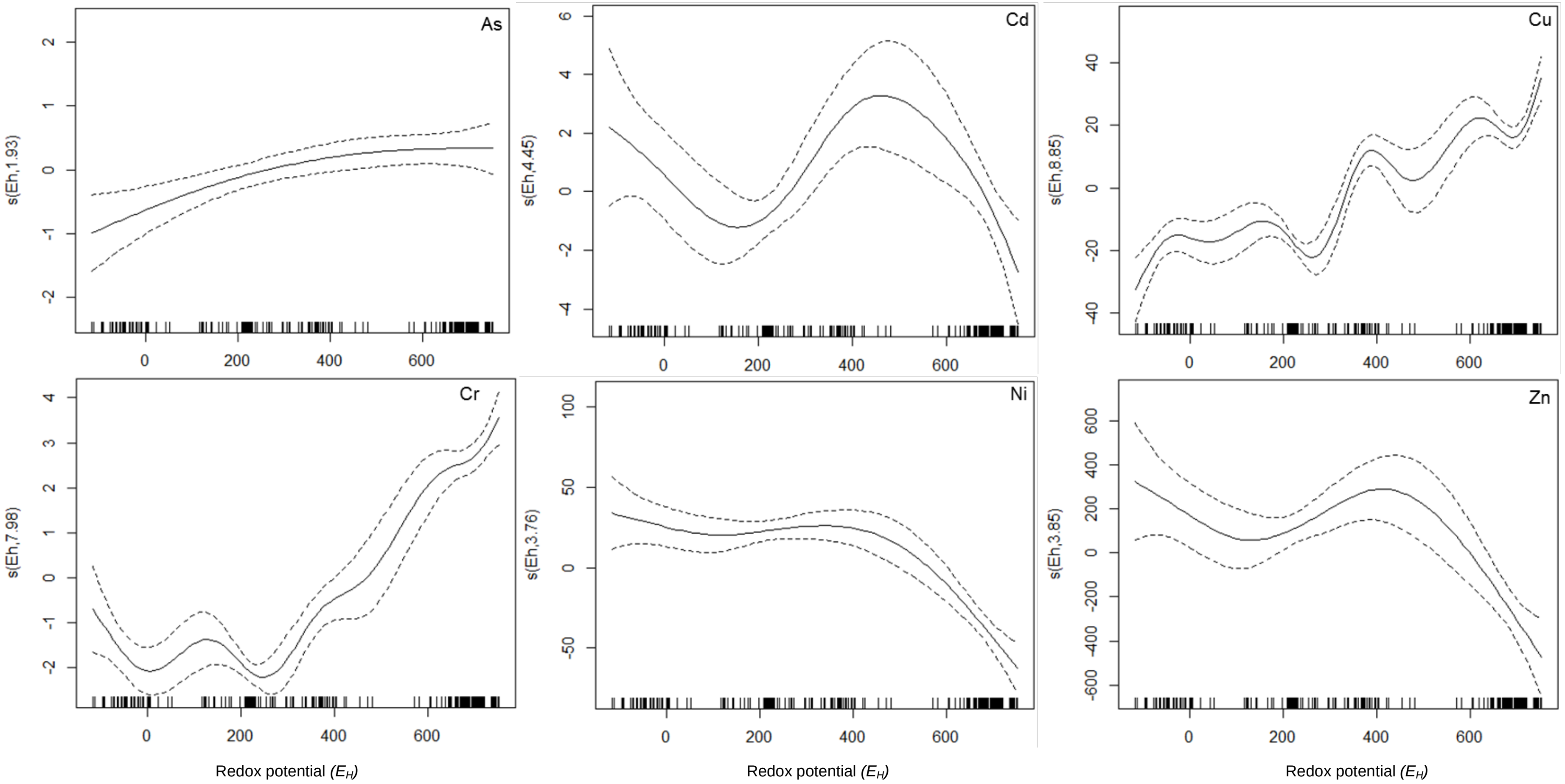



## Appendix B1

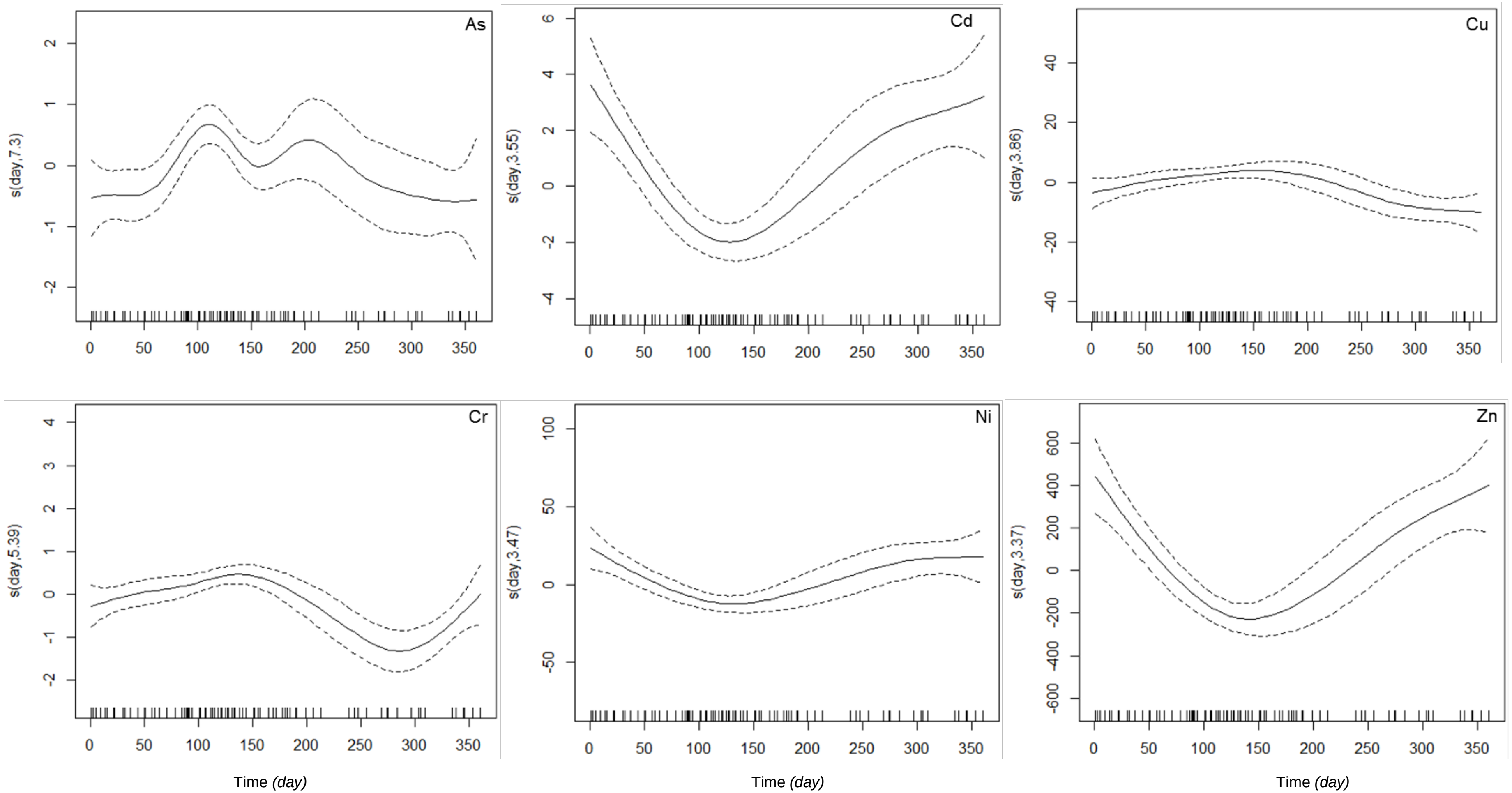
Smoothers and 95% pointwise confidence bands from the plot combined GAMs.

*Significant relations between TMs and $E_H$ (x-axis) were detected for As ($P<0.01$, $F=5.87$); Cd ($P<0.01$, $F=3.05$); Cu ($P<0.001$, $F=60.46$); Cr ($P<0.001$, $F=39.59$); Ni ($P<0.001$, $F=24.82$) and Zn ($P<0.001$, $F=9.89$). Estimated degrees of freedom are given in the y-axis label*



## Appendix B2

Smoothers and 95% pointwise confidence bands from the plot combined GAMs.
*Significant relations between TMs and day (x-axis) were detected for As (P<0.01, F=3.17); Cd (P<0.001, F=9.39); Cu (P<0.001, F=5.65); Cr (P<0.001, F=6.92); Ni (P<0.001, F=6.67) and Zn (P<0.001, F=13.49). Estimated degress of freedom are given in the y-axis label*



Chapter 4

# Simulation of wet-dry cycles in three floodplain soils and their effects on the release of As, Cd, Cu, Cr, Ni, and Zn

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*Ready for submission*

## Abstract

Wet-dry cycles are determinants for the characteristic spatial mosaic of habitats and additionally for the temporal changing processes within floodplain soils. River-floodplain ecosystems are already known to be long-term sinks for certain contaminants, and yet even small changes of the frequency, magnitude, and timing of the drying and rewetting of floodplains can episodically turn them into a source for matter. Within climate change it has been proposed that strong fluctuations between floods and droughts will occur more frequently, which may result in changing of the biogeochemical conditions of floodplain soils. By using biogeochemical microcosms we were able to simulate successive anaerobic (simulated wet) to aerobic (simulated dry) cycles to monitor the impact of such strong fluctuations on soil biogeochemistry and related trace metal dynamics. We investigated the effects in three hydro-geomorphologic units typical for floodplains: levee, depression, plateau, and could identify different release patterns for each of them. The low buffered soil showed steadily increasing dissolved concentrations of Cd, Cr, Ni, and Zn, whereas Cd, Cu, Cr, and Zn in the high buffered soil reached a maximum concentration that decreased again. The medium buffered soil showed peak values (As, Cd, Cu, Cr, Ni) and then slightly increased (Ni, Cu) or constant (Cd, Cr) amounts throughout the experiment. However, Fe and S could be identified as important factors which determined trace metal dynamics in the studied soils; concentrations of As, Cu. Cr, Ni, and Zn increased with increasing Fe-concentrations whereas Cd, Cu, Cr, Ni, and Zn seem correspondingly to be dependent on S that went along with the course of the wet-dry cycle. Thus characteristics of the whole catchment area need to take into consideration for floodplain management activities since esp. spatial as well as temporal uncertainties may exist. Moreover, further detailed research including the speciation of metals is recommended. Harmful changes with view to the mobility of As, Cd, Cu, Cr, Ni, and Zn are assumed to occur in floodplain soils which should be recognised and monitored on a longer term to prevent environmental damage and costs. Moreover this could allow ecologically and socio-economically sound use and management of floodplain soils against the background of adaptation and mitigation strategies for climate change.


### 4.1 Introduction

Floodplains are characterised by a spatial mosaic of habitats changing over time, primarily due to flooding and related processes where wet-dry cycles can be observed (Tockner et al. 2010). The drying and rewetting of floodplains affect redox processes such as oxidation and the reduction of Fe and Mn in combination with changes in pH-value, S-cycling, the presence of complexing agents such as dissolved organic carbon (DOC) and microbial activity. These are some of the most important factors determining the retention and remobilisation of pollutants within floodplains and across river-floodplain gradients (Du Laing et al. 2009, Schulz-Zunkel and

Krueger 2009, Rinklebe and Du Laing 2011). Floodplain-river-systems are known as long-term sinks for contaminants (e.g. Eisenmann 2002, Lair et al. 2009). However, even small changes to the frequency, magnitude, and timing of drying and rewetting can result in large shifts in the net ecosystem exchange, making floodplains a periodic source of matter, including trace metals (Tockner et al. 2010). Recently, it has been proposed that strong fluctuations between floods and droughts will occur more frequently under the influence of climate change (EEA 2012). Such changes may influence the physico-chemical and biogeochemical conditions in soils, which control the availability (Poot et al. 2007), the transport and deposition of sediment and associated trace metals (TMs) (Thonon et al. 2006). At the same time the PRESS-report (Maes et al. 2012) highlights the potential of wetlands, rivers, streams, and lakes to remove or immobilise pollutants and provide clean water for multiple uses, lowering the cost of wastewater treatment that is based solely on technological solutions. The total content of TMs in soils does not provide sufficient information about potential environmental risks (Joubert et al. 2007). Therefore, it is essential to assess TMs in the soil solution to describe TM behaviour in soils (e.g. Frohne et al. 2011, Schulz-Zunkel et al. 2013) and contaminant bioavailability and toxicity that are a result of complex interactions between nutrients, hydrology, and pollutant levels (Lair et al. 2009). Little is still known however about the fate and dynamics of dissolved TMs and those factors determining TM dissolution in spatially and seasonally variable freshwater environments, especially during wet-dry cycles. Moreover, a description of such complex interactions is rare (Tiktak et al. 1998, Sauve et al. 2000, Smolders et al. 2009) and thus it is not fully understood whether and to which extent TMs may be dissolved during such cycles. Furthermore, less information is available on whether an increase in dissolved TMs will remain in a solution beyond an expected time (e.g. beyond anaerobic phases) and thus possibly demonstrating a behaviour that is time-delayed and non-linear (Salomons 1998). Soil microcosms (Patrick et al. 1973) are ideal experimental set-ups for simulating environmental conditions in the laboratory. With such an apparatus it is possible to adjust aerobic (high $E_H$) and anaerobic (low $E_H$) conditions by adding gaseous $O_2$ or $N_2$ to incubated soils. It also allows for changes in pH-value and for collecting samples under those simulated conditions. To simulate wet-dry cycles we used an automated biogeochemical microcosm set-up. This system was already described by Yu and Rinklebe (2011) and has been successfully used in previous studies for investigating trace gases (Yu et al. 2007), for quantifying mercury emissions (Rinklebe et al. 2010), for mercury methylation (Frohne et al. 2012), and for determining the dynamics of trace metals (Rupp et al. 2010, Frohne et al. 2011). We chose soils from three different hydro-geomorphological units (levee, depression, plateau), which are typical and representative for the heterogeneity within floodplains in terms of habitat, flooding frequency, degree of pollution and soil properties. We conducted two simulated successive cycles under aerobic and anaerobic conditions and specifically investigated the effects of such simulated wet-dry cycles and changing biogeochemistry on the release of TMs (As, Cd, Cu, Cr, Ni, Zn) within these three soils. We used generalised additive models (GAMs) to study how TM release might be related to $E_H$, pH, Fe, Mn and S. Because sulfides are formed by the microbial reduction of sulphate when organic matter decomposes, we also included DOC and moreover nitrate-nitrogen the origin of which might serve as an indicator for microbial activity (Peterson et al. 1997). Moreover, we aimed to explore how sampling time (fSN) and spatial heterogeneity (fplot) between the three studied soils would influence the release of TMs and thus included these variables into the model. More specifically, we wanted to assess a) whether GAMs are suitable for explaining the variation of TM release during the simulation experiment, b) how TM release is related to $E_H$, pH, Fe, Mn, S, DOC, $NO_3$-N and c) the relative importance of these factors influencing the release of TMs from the soils under investigation.

## 4.2 Materials and methods

### 4.2.1 Research area

The research area 'Schönberg Deich' is a floodplain segment along the German Middle Elbe region. It is used as a hay meadow and for cattle-grazing and is situated within a meander loop that encompasses a floodplain of ca. 200 ha on the left of the river Elbe. The river Elbe itself is the third largest river in Central Europe, in terms of its length and the size of its catchment area. High water levels mainly occur in spring because discharge from the river Elbe is mainly influenced by snow melt (Scholten et al. 2005). Several sections of the river Elbe and its floodplains have remained semi-natural. Channelling of the river Elbe has not taken place and only a few meanders have been straightened. However, it has lost a majority of its floodplains. Those that do remain are regularly inundated and thus able to maintain wetland and floodplain forest habitats that are unique within central Europe (after Adams et al. 2001). Within the research area we located three study plots that can be regarded as typical hydro-geomorphological units within floodplains: (levee, plateau and depression) while at the same time representing a topographical as well as pollution gradient from slight (levee) via medium (plateau) to high (depression) flooding frequency, flood duration and pollution level (Fig. 4.1). The basic soil properties and TM content of the soils under investigation are presented in Table 4.1.

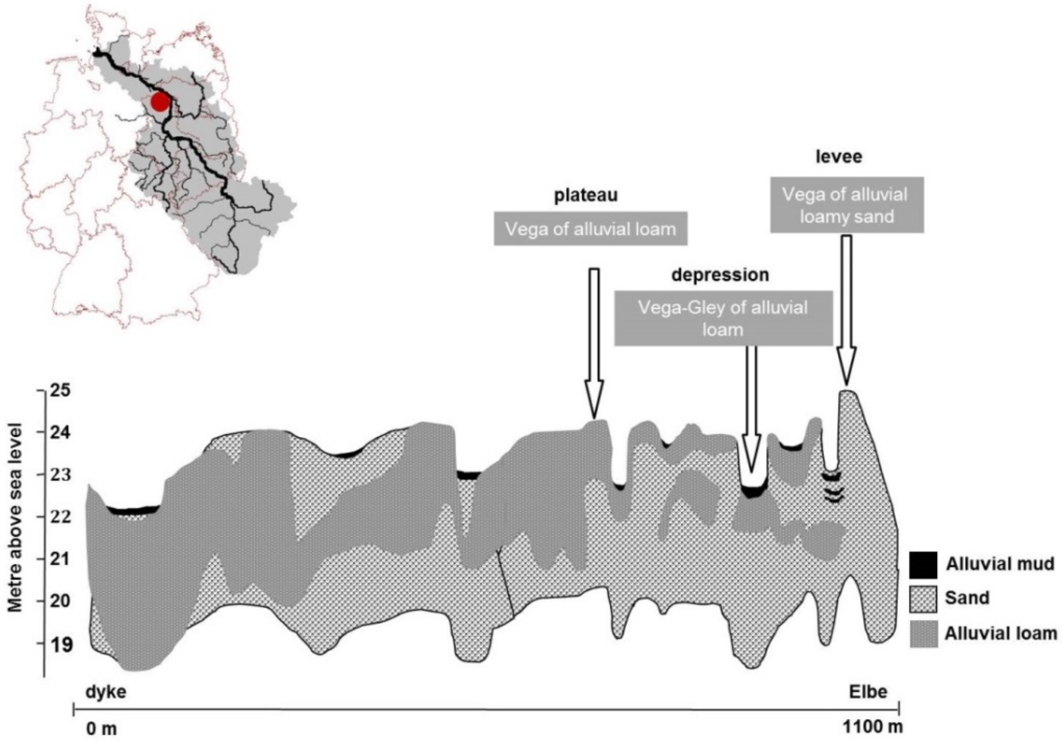



Figure 4.1 The research area 'Schönberg Deich', its location in the Elbe catchment and a segment of the profile with the location of the studied plot's (adapted from Krueger et al. 2004a)

*Table 4.1a Characteristics of the studied soils - site and soil characteristics*

| | | *site and soil characteristics* | | |
|---|---|---|---|---|
| Plot name | | **DS** | **LS** | **PS** |
| Depth | cm | 0-10 | 0-10 | 0-10 |
| Soil type[1] | | Alluvial gley (Vega-Gley) of alluvial loam | Alluvial brown soil (Vega) of alluvial loamy sand | Alluvial brown soil (Vega) of alluvial loam |
| Soil type[2] | | Eutric Gleysol (GLe) | Eutric Fluvisol (FLe) | Eutric Fluvisol (FLe) |
| Horizon[1] | | aAh | Ah | aMAh |
| Particle size[1] | % | Clay:19.4, silt: 71.7, sand:8.9 | Clay:9, silt: 25, sand:66 | Clay:18.3, silt:45.7, sand:35.9 |
| $KAK_{eff}$[3] | $cmol_c/kg$ | 22 to < 30 | 14 to < 22 | 17 to < 21 |
| Total Carbon (TC) | % | 7.7 | 4.1 | 3.4 |
| Total Nitrogen (TN) | % | 0.6 | 0.3 | 0.3 |
| Extractable Carbon ($C_{hwe}$) | *mg/100g* | 263 | 256 | 215 |
| Extractable Nitrogen ($N_{hwe}$) | *mg/100g* | 19.0 | 17.1 | 16.9 |
| pH-value | $CaCl_2$ | 5.12 | 3.91 | 4.56 |
| Metre above sea level (masl) | *m* | 22.8 | 24.9 | 24.3 |
| Distance to the river Elbe | *m* | 138 | 25 | 307 |
| Position to mean water level | *m* | 0.9 | 3.0 | 2.4 |

[1] *German soil classification according to KA5 (2005)*
[2] *International soil classification according to* IUSS-ISRIC-FAO (2006)
[3] *estimated according to KA5 (2005), sum of $KAK_{pot}$ particle size and $KAK_{pot}$ humus*

*Table 4.1b  Characteristics of the studied soils – trace metals*

| | ***Trace metals[4]*** | | |
|---|---|---|---|
| **ICP-MS** | Aqua Regia extracted [µg/g]* | | |
| **As** | **75** | 14.3 | **35** |
| **Cd** | 7 | 0.42 | 2.1 |
| **Cu** | 300 | 42 | 117 |
| **Cr** | 360 | 64 | 166 |
| **Ni** | 340 | 38 | 116 |
| **Zn** | 1310 | 77 | 470 |
| **ICP-MS** | Ammonium Nitrate extracted [µg/l]# | | |
| **As** | **24** | **16** | **12.6** |
| **Cd** | **250** | **91** | **100** |
| **Cu** | **240** | **132** | **122** |
| **Cr** | 18 | 16 | 10.7 |
| **Ni** | **840** | **990** | **830** |
| **Zn** | **18000** | **8500** | **15000** |
| **ICP-MS** | Water extracted [µg/l]# | | |
| **As** | **24** | **28** | **12.2** |
| **Cd** | 2.7 | 3.8 | **8.4** |
| **Cu** | **200** | **93** | **140** |
| **Cr** | 11.1 | 26 | 7.1 |
| **Ni** | 47 | **51** | **74** |
| **Zn** | 370 | **550** | **850** |

*[4] Bold: threshold exceedance regarding the German Soil Protection Guideline (BBodSchV 1999)*
** action value for grasslands, #pathway soil-groundwater*

### 4.2.2 Soil sampling, pre-treatment and analysis of the sampled soils

Soil horizons were collected from the Ah- (levee, depression) and the aMAh-horizon (plateau). Since laboratory investigations were carried out in three replicates, soil material was collected with the aim of pooling it to one composite sample for each horizon. Soil material was homogenised, air-dried and sieved <2 mm. Soil properties were determined according to standard methods (Schlichting et al. 1995) as follows: Total C (Ct) and Nt were measured with dry combustion and thermal conductivity detection using a C/N/S-Analyser (Vario EL Heraeus, Analytik Jena, Germany). Particle-size distribution was determined by wet-sieving and sedimentation using the pipette-sampling technique. Soil pH-value was measured in a $0.01MCaCl_2$-solution mixed at a ratio of 2.5:1 with soil. Total metal and As concentrations of the soil were quantified following extraction using aqua regia, ammonium nitrate and water.

### 4.2.3 Soil microcosm set-up, soil suspension sampling and analysis of the soil suspension samples

Three replicates of each soil were incubated (soil–water ratio: 1:8) in the biogeochemical microcosms. A platinum (Pt) electrode with a silver–silver chloride (Ag/AgCl) reference electrode was used for the $E_H$ measurement whereas a pH electrode was used for the pH-value measurement. Redox potential and pH-value in the soil suspension of each microcosm were automatically monitored every 10 min. Data recorded by the sensors were collected using a data logger. The simulation of the two succeeding cycles from anaerobic (simulated wet) to aerobic (simulated dry) cycles took place by adding $N_2$ (to reach lower $E_H$) and $O_2$ (to raise $E_H$) through an automatic valve-gas regulation system. The experiment was conducted over 85 days, during which we took nine soil suspension samples at defined $E_H$ levels (sampling number (SN) 1: starting point; SN2, 6: ca. 200 mV; SN3, 7: ca. 0mV; SN4, 8: minimum negative redox value; SN5, 9: maximum positive redox value). These samples (20mL each time) from each microcosm were immediately filtered through a 0.45µm millipore membrane (Whatman Inc., USA) into two 10-mL test tubes. One sub-sample was used to monitor concentrations of DOC that was analysed after combustion of the finely-sprayed suspension with a micro N/C analyser (Analytik Jena AG, Germany). To the other sub-sample, 3 drops of 2M $HNO_3$ were added to preserve the solution for later analysis. Concentrations of TMs in the soil suspension were analysed on ICP-MS using an ELAN 5000 (PerkinElmer, Shelton, CT, USA). Furthermore, we analysed the soil suspension for Fe, Mn, S and $NO_3$-N with an ion chromatograph (IC 120, Dionex, USA).

### 4.2.4 Data analysis and generalised additive modelling

For data exploration and to identify which statistical analyses are useful, we followed Zuur et al (2010). For the analysis we averaged the logged data of $E_H$ and pH-value per day. For all other variables the measured values per sampling number and per replicate were used. We selected As, Cd, Cu, Cr, Ni and Zn as TMs for the analysis. We measured total concentrations in the soil suspension. For data exploration we first plotted the simulated curves of $E_H$ and pH-value against time and SN separately for the three soils (Fig. 4.2). In addition we used box plots to be able to identify the differences of the dissolved TM concentrations per SN (Fig. 4.3A) and between the three soils (Fig. 4.3B). To identify differences of TM release between the soils, we used scatter-plot smoothing to fit a non-parametric smoothed curve through the data. We used two different span widths; 0.2 to maintain the current course of dissolved TMs and 1.0 to get a more general interpretation of TM dissolution during the experiment (Fig. 4.4). To interpret the effects of anaerobic (simulated wet) to aerobic (simulated dry) cycles on TM release we used generalised additive models (GAMs) because relationships between TMs and the explanatory variables ($E_H$, pH, DOC, Fe, Mn, S, $NO_3$-N) are dominated by non-linear or even rather unclear humped-shaped relationships. Moreover, we were able to recognise a pattern in the course of the dissolved TMs in relation to temporal (fSN) as well as area-specific variables (fplot). A generalised additive model fit a smoothing curve through such data and allows non-linear relationships between response and multiple explanatory variables (Zuur et al. 2009). Since we only had a small amount of complete data sets (n=81), we pooled the data for the three different soils into one data table, aware of the fact that we were putting together different spatial characteristics. To detect correlations between the explanatory variables we used multiple scatter plots as well as the variance inflation factor (VIF) (Zuur et al. 2010). Strongly-correlated predictors had to be excluded from the analysis or, as in the case of $E_H$ and pH which are both assumed to have high explanation power of the variance of dissolved TMs, were modelled separately. We built distinct models for each TM. To account for possible spatial effects we included the soils under investigation as factors in the model (fplot). Moreover, we also included the sampling number (fSN), defined as a random effect, to account for the correlation of observations throughout the duration of the experiment. The full data sample was used for both, model fitting and model selection. The explanatory variables were selected using a stepwise model selection criterion, starting from fitting a full GAM in which all explanatory variables were included. The procedure omits the variable with the highest P-value if greater than 0.1 (thus having no significant effect) at each step and evaluates the alternative model by comparing the Akaike's Information Criterion (AIC). If the alternative model has a lower AIC than the full model, the variable is to be excluded from further modelling. The model with the lowest AIC was selected and reported. The fitted, full starting models that we used are given below:

Equation 1:

$$TMi \ = \ \alpha i \ + \beta i + \ \mathrm{fi}\ (E\hbar) \ + \ \mathrm{fi}\ (DOC) \ + \ \mathrm{fi}\ (Fe) \ + \ \mathrm{fi}\ (Mn) \ + \ \mathrm{fi}\ (S) \ + \ \mathrm{fi}\ (NO3) \ + \\ factor\ (SN, bs = \text{"}re\text{"}) \ + \ factor\ (plot) \ + \varepsilon i$$

Equation 2:

$$TMi = \ \alpha i \ + \beta i + \ \mathrm{fi}\ (pH) \ + \ \mathrm{fi}\ (DOC) \ + \ \mathrm{fi}\ (Fe) \ + \ \mathrm{fi}\ (Mn) \ + \ \mathrm{fi}\ (S) \ + \ \mathrm{fi}\ (NO3) \ + \\ factor\ (SN, bs = \text{"}re\text{"}) \ + \ factor\ (plot) \ + \varepsilon i$$

$TM_i$ is the response variable and stands for the various TMs (As, Cd, Cu, Cr, Ni, Zn), $\alpha$ is the intercept, $\beta$ is the slope, $f(X_i)$ stands for the various explanatory variables ($E_H$, pH, DOC, Fe, Mn, S, $NO_3$-N), and the factor sampling number *(fSN)* is defined as a random effect (bs="re"). Statistical analyses were performed with the packages mgcv, nlme, lattice, using R (version 2.14.2; R Development Core Team, 2011).

### 4.2.5 Model validation

The selected models were tested for violation of homogeneity (fitted against residual values), independence (residual values against all covariates), influential observations (cooks distance) and normality (histograms). These plots were diagnostic tools to see how well the statistical model fit the data, whether it had to be improved, and to compare the fit of different models. The 'goodness-of-fit' of the selected models was also evaluated by the deviance explained and the total degree of freedom.

## 4.3 Results

### 4.3.1 Simulated wet-dry cycles in different floodplain soils

By using soil microcosms we simulated two successive wet-dry-cycles in three different floodplain soils to investigate how TM release might be affected by rapidly-changing conditions within the soils.

Figure 4.2A shows the course of $E_H$ during the experiment in the three different soils. Until 200mV were reached (first wet cycle) the three soils behaved comparably, but after that $E_H$ within the soil of the plateau (PS) and the depression (DS) decreased faster than within the levee soil (LS), obtaining the lowest $E_H$ values on day 22, whereas the LS reached its lowest $E_H$ value on day 29. During the second wet cycle DS and PS still showed a very similar behaviour and responded immediately to the $E_H$ decrease whereas LS now lagged even further behind the others. Only DS reached the former lowest $E_H$. Overall the maximum negative $E_H$ diverted between the three soils (LS: -90mV to 507mV, DS: -172mV to 535mV, PS: -144mV to 526mV). Since pH-value usually corresponds with $E_H$ these values differ between the three soils and during the experiment, too (LS: 4.4 to 5.8, DS: 5.5 to 6.9, PS: 4.9 to 6.7). However, former pH-values were not reached again by the end of the experiment; pH-values within the LS remained rather low throughout the whole experiment (Fig. 4.2B). Due to these differences over the course of the $E_H$, sampling days between the plots varied and followed the line: DS<PS<LS until SN5, from SN6 onwards: PS<DS<LS, whereas the row PS<DS/LS only represented SN8 and SN9 (Fig. 4.2A) due to a lack of sampling material for PS.

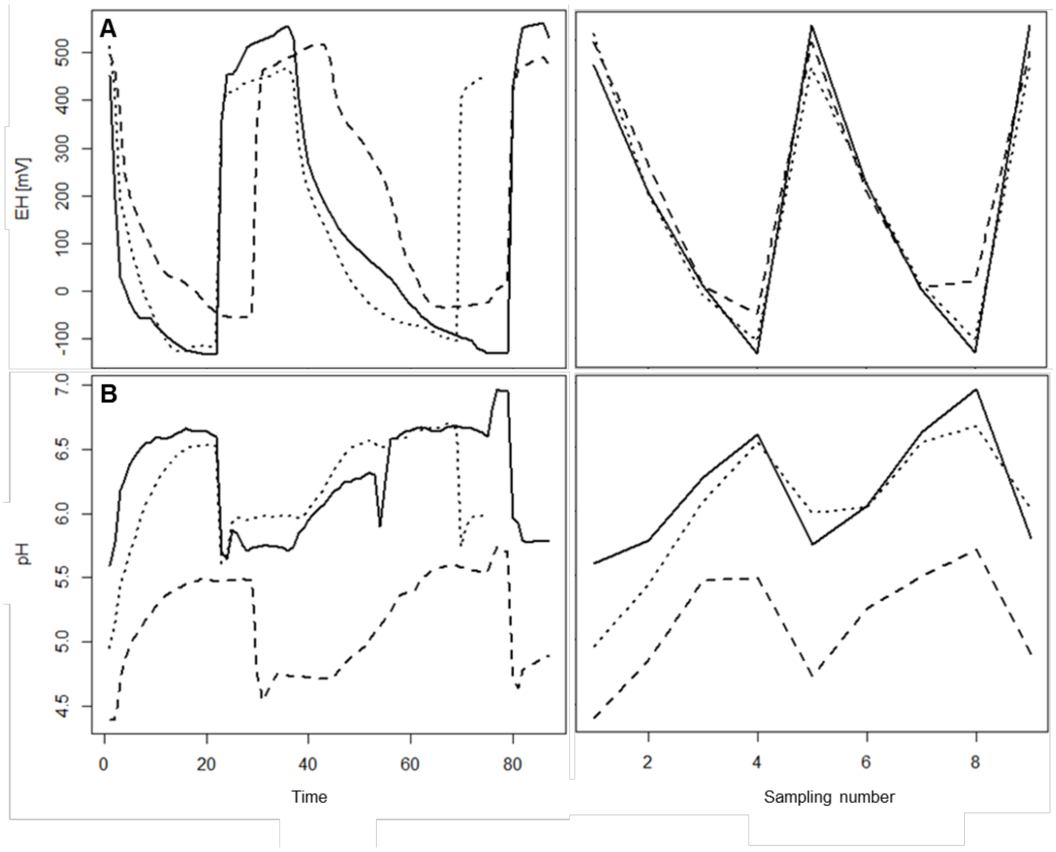
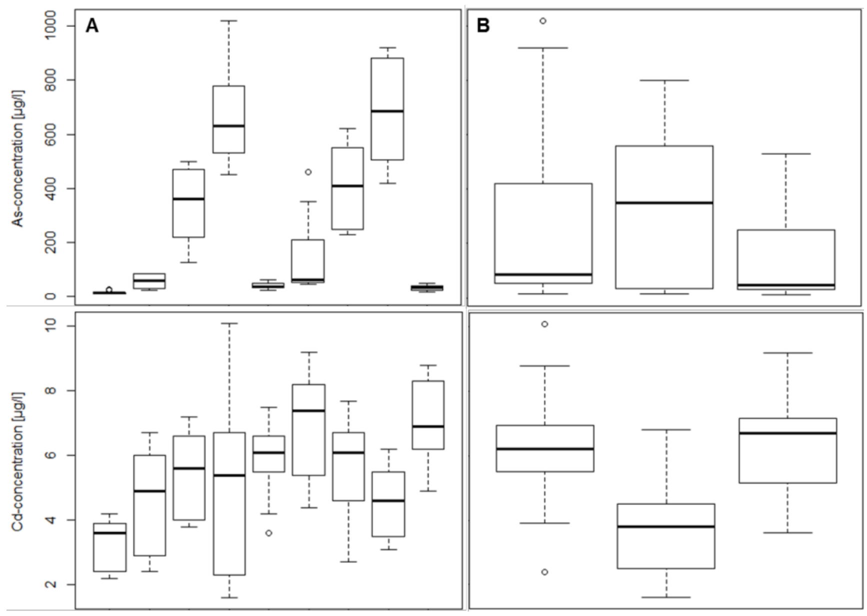



Figure 4.2 Redox curve (A) and pH curve (B) related to the duration of the experiment and to the sampling points for the three studied soils
*(DS=solid line, PS=dotted line, LS=dashed line)*

### 4.3.2 Amount of trace metal release during wet-dry cycles

Release of TMs in floodplain soils are strongly determined by changing water levels within soils mainly caused by changing water levels from an adjacent river. Figure 4.3 shows the variation in the dissolved amounts of TMs on different sampling dates (A) and between different soils (B). Even if the variation within one sampling number is very high, a clear pattern over the course of the experiment can be identified for each TM. However, an interpretation of those patterns related to the course of the simulated wet-dry-cycles, is difficult. Only dissolved As-concentration went significantly with the simulated wet-dry cycles increasing during wet phases (SN=4, 8) for all three soils. However, there is still a visible trend that dissolved amounts of Cd, Cu and Zn deceased under anaerobic conditions whereas those of Ni decreased under aerobic conditions (SN=5, 9). On the contrary, the concentration of dissolved Cr increased steadily until SN=3 ($E_H$=ca. 0 mV) and remained almost constant until the end of the experiment. For all TMs dissolved concentrations were higher at the end compared to the beginning of the experiment. Threshold values (soil-groundwater pathway) according to the German Soil Protection Guidelines (BBodSchV 1999) were exceeded for all soils, although the highest maximum dissolved concentrations were found within the LS (Cr, Ni, Zn) and the DS (As, Cd, Cu). Furthermore, variations within and between the soils were very high. The median shows an order of the soils under investigation in terms of dissolved TM concentrations; LS > DS > PS (As, Cr), LS > PS > DS (Ni), LS > DS, PS (Zn), PS > DS > LS (Cd), DS > PS > LS (Cu).



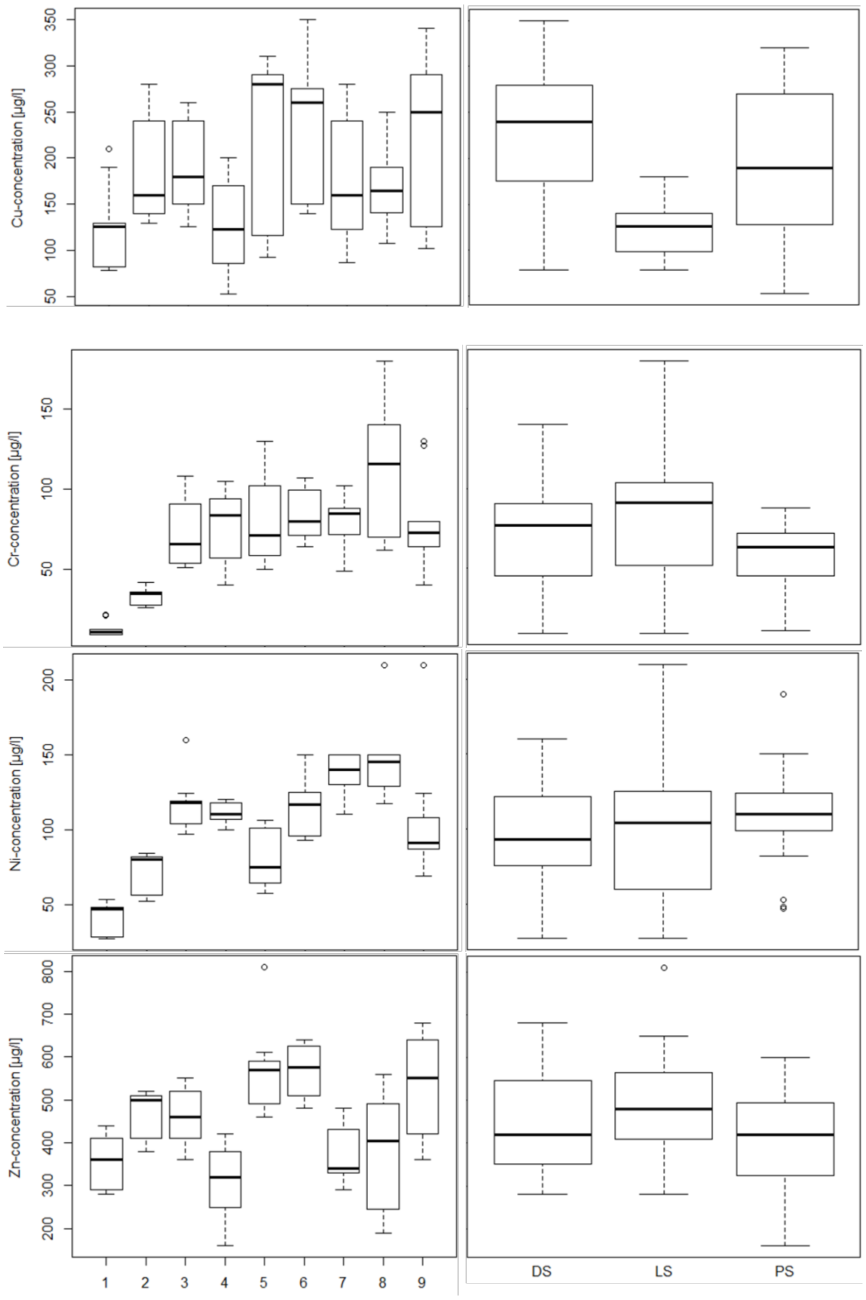



Figure 4.3 Dissolved amounts of TMs at the different sampling dates (A) and within the different soils (B). The boxplots show maximum, minimum, median values and outliers for the several TM concentrations during the simulation experiment.

However, Figure 4.4 shows that TM release patterns could be identified for the three soils individually. Within the LS, dissolved concentrations of Cd, Cr, Ni and Zn steadily increased from the beginning to the end of the experiment, whereas Cd, Cu, Cr and Zn increased to a maximum level in DS, around the middle of the experiment, after which they slightly decreased again. Dissolved amounts of As, Cd, Cu, Cr and Ni within the PS increased until half way through the experiment and then only increased very slightly from that point until the end of the experiment.

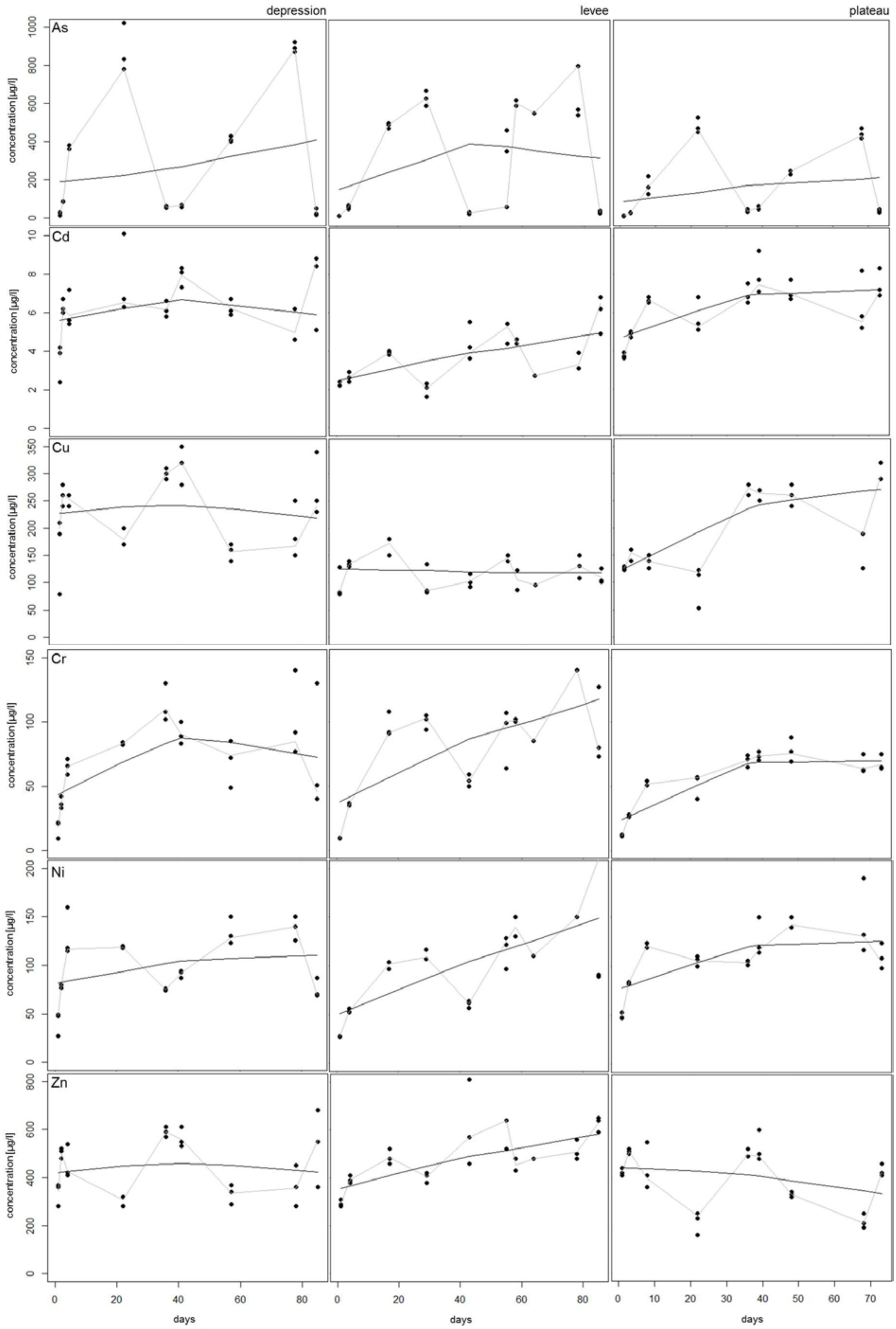
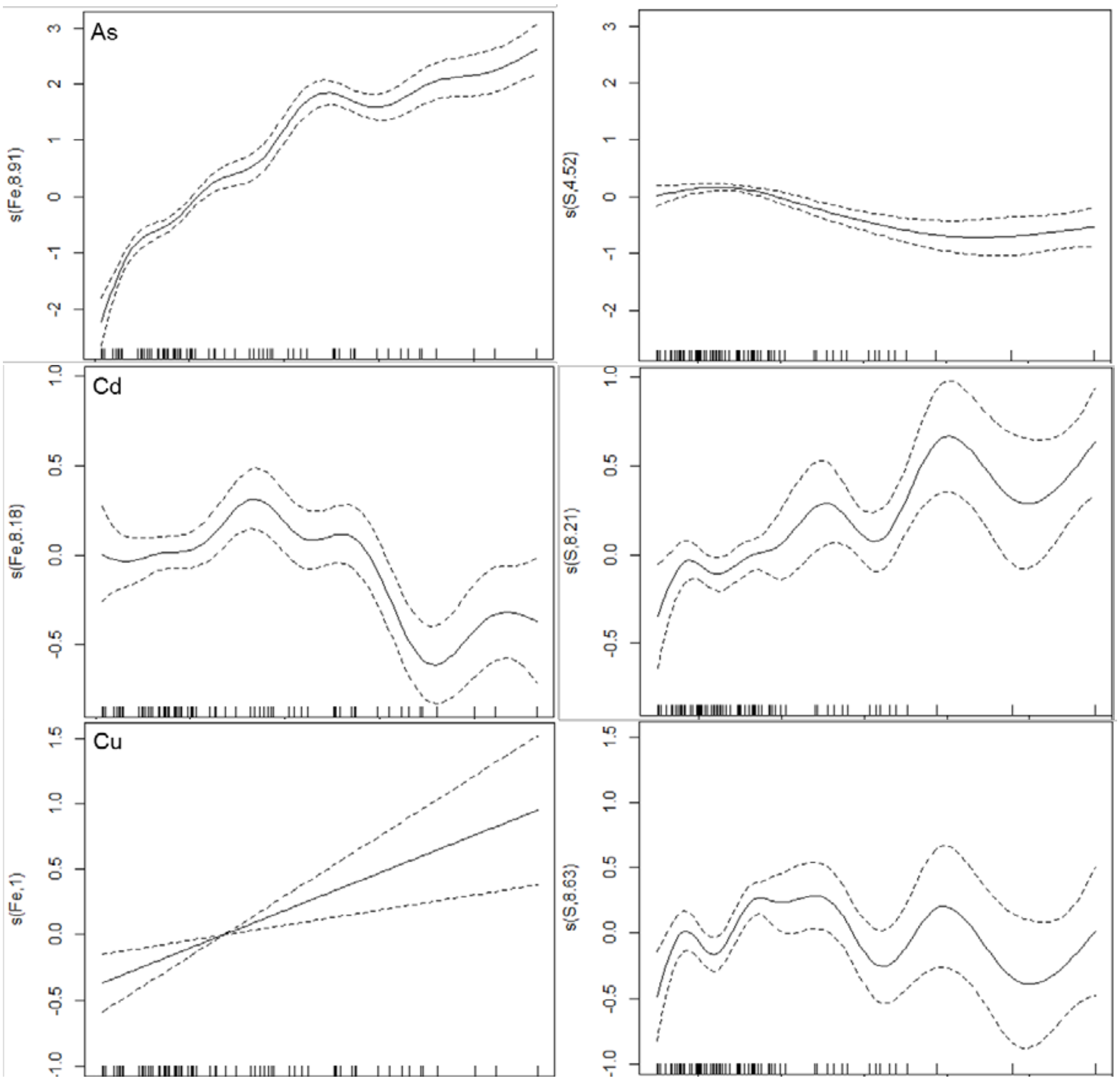



Figure 4.4 Trace metal release patterns during the experiment, visualised with smoothed curved with two span width *(grey line= span width 0.2, black line= span width 1)*

### 4.3.3 Explaining the variation of TM dissolution depending on wet-dry cycles

The GAMs showed a great potential to interpret the relationship between TM release and the monitored biogeochemical characteristics of the three soils. Annex A provides the results of the final models for each TM. The explained deviance of the models ranged from 86.5 to 99.5 %. Moreover, the model validations suggest that the model fitted the observed data reasonably well. Generally, the models that included pH-value as an explanatory variable instead of $E_H$ were slightly better. However, the GAMs relating TMs to selected soil parameters showed complex responses. Spatial characteristics of each soil type under investigation (fplot) seem to be crucial for TM release in the case of As, Cd, Ni and Zn. Out of all of the models, S and Fe were found to be significantly influential on TM release in every model. Broadly speaking, increasing Fe-concentration led to an increase in TM release, except for Cd. On the contrary, dissolved TM concentrations (excluding As and Ni), showed an up and down trend in relation to S concentrations (Fig. 4.5).



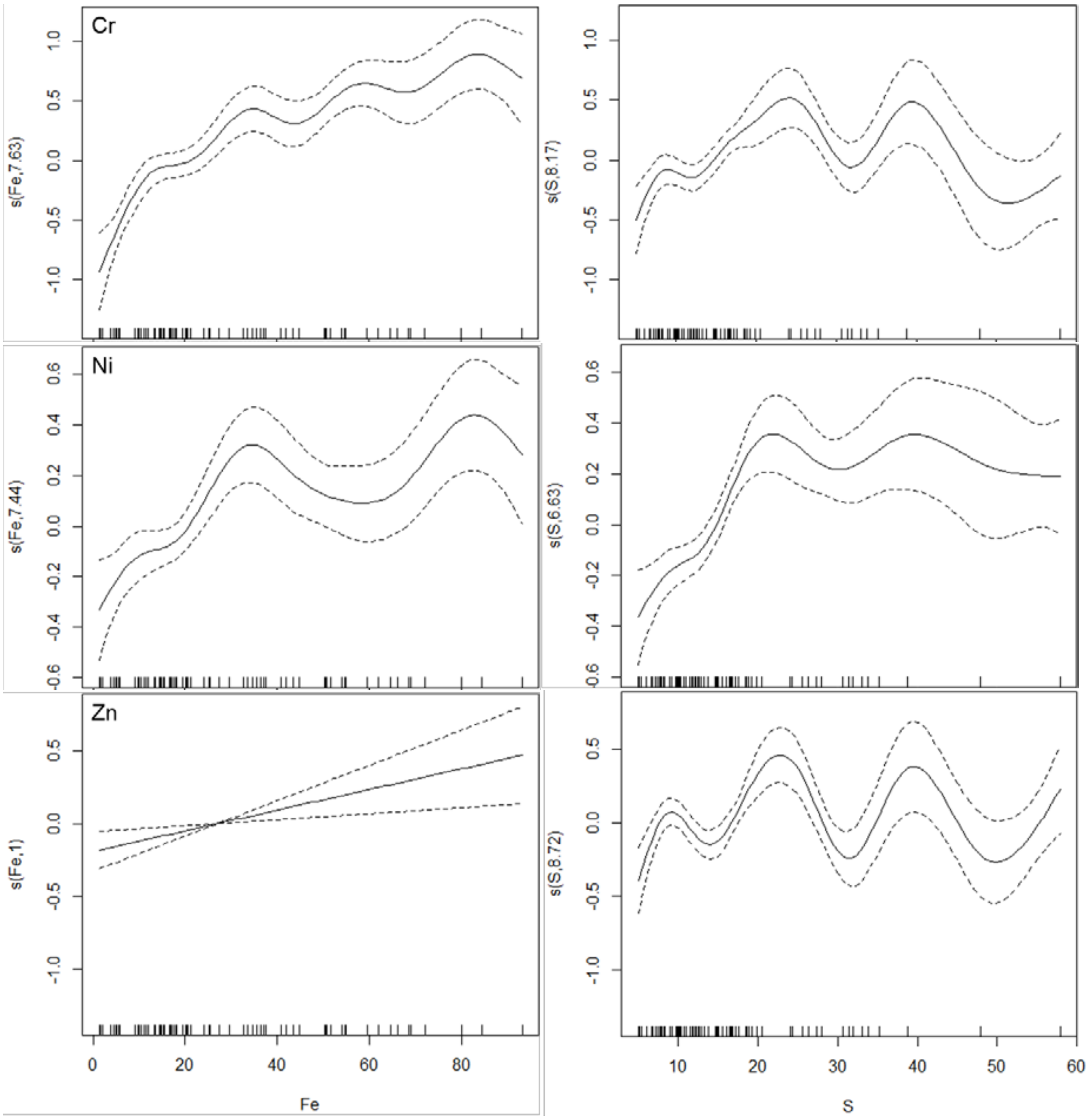



Figure 4.5 Smoothers and 95% pointwise confidence bands of the several GAMs for each TM

*For all studied TMs Fe and S were significant: As (Fe: $P< 0.001$, $F =51.66$ , S: $P<0.001$, $F=10.94$); Cd (Fe: $P< 0.001$, $F=9.60$, S: $P<0,01$, $F=3.67$); Cu (Fe: $P< 0.01$, $F=11.19$, S: $P<0.001$, $F=4.66$); Cr (Fe: $P<0.001$, $F=11.38$, S: $P<0.001$, $F=5.15$); Ni (Fe: $P<0.001$, $F=4.43$ , S: $P<0.001$, $F=5.88$) and Zn (Fe: $P < 0.01$, $F=7.97$, S: $P<0.001$, $F=5.81$). Estimated degrees of freedom are given in the y-axis label.*

## 4.4 Discussion

### 4.4.1 Simulated wet-dry cycles in different floodplain soils

Floodplains are naturally a complex mosaic of habitat patches (Tockner et al. 2010) and therefore display strong spatial as well as seasonal heterogeneity, including retention and remobilisation processes of TMs (e.g. Eisenmann 2001, Schwartz 2001, Rinklebe et al. 2007, Schulz-Zunkel et al. 2013). Little is still known about how strong redox fluctuations due to flooding and drying may influence TM retention or release from floodplain soils.

This is particularly because of a high dependency of such processes on the existing small-scale varying topography and that these may be affected much differently by hydrological changes (see Poot et al. 2007, Schulz-Zunkel et al. 2013). Here obvious different effects were also found from simulated wet and dry conditions on $E_H$ in the three different soils. Possible explanations are different redox sensitivities in soils depending on the duration of high water phases as well the presence of organic matter (OM) and specifically extractable carbon ($C_{HWE}$) (Heinrich et al. 2000). Moreover, the content of soil organic carbon $C_{org}$ might be able to serve as a rough indicator of potential microbial activity ($C_{mik}$) (Rinklebe 2004) and thus for the redox sensitivity of soils. However, although a significant correlation was found between $C_{mik}$ and $C_{org}$ , especially in floodplain soils (Rinklebe et al. 2001), not all parts of $C_{org}$ are available for microorganisms (MO). Thus, $C_{HWE}$ (Tab. 4.1) was assessed since this fraction can easily be converted by MOs(Körschens et al. 1990). These values showed that the investigated soils are assumed to have a very high potential for microbial activity (Rinklebe and Langer 2006). However, in terms of $C_{org}$ as well as $C_{HWE}$ the three soils range in the order: DS>LS>PS. Redox potential decreased within LS with a delay of seven days during the first wet cycle, compared to DS and PS and therefore does not tie in with assumptions based on the carbon content. This performance is also true for the second wet cycle in which the time delay within LS is adopted. Moreover, $E_H$-values reached higher negative values within DS and PS than in LS. From these findings we assumed that within LS the duration of the simulated wet-dry cycle played a more important role and thus probably indicated the length of time that the population of bacteria required to grow. Beyond that, even if $C_{org}$ and $C_{HWE}$ favour microbial activity and thus redox sensitivity, the very low pH-value might inhibit microbial activity in this particular soil.

### 4.4.2 Amounts of trace metal dissolution during the simulated wet-dry cycles

It is well known that TM dissolution is affected by a number of soil properties including pH, $E_H$, OM as well as the type and amount of clay minerals, iron-, manganese- and aluminium- oxides; high total TM concentrations will have a much smaller effect in calcareous soils than in more acidic soils, because the metals are not very mobile; DOC usually increases with decreasing $E_H$ favouring complex amounts of TMs in soil solutions as well as suspensions (Schulz-Zunkel and Krueger 2009). During the experiment $E_H$ and pH-value were manually controlled. However, from the course of dissolved Cd, Cu, Cr, Ni, Zn during the experiment it is expected that a combination of several soil parameters will affect TM dissolution in the soil suspension, possibly leading to unexpected releases of TMs as might be predicted from the total TM content in soils. By comparing the concentrations of dissolved TMs between the three soils we identified maximum values per TM either in DS (As, Cd, Cu) or in LS (Cr, Ni, Zn). For the latter, this was very unexpected since here total TM concentrations in the soils are even lower than the threshold values provided by the BBodSchV (1999) and thus this soil is obviously less polluted compared to DS and PS. However, water and especially ammonium-nitrate extractable TM concentrations (Tab. 4.1) lead to the expectation that higher amounts of TMs could be remobilised from LS during flooding events. At least for Zn comparable results were found for a levee soil *(Norm-Vega)* along the lower Middle Elbe (Schwartz 2001). In this work it is assumed that the combination of total Zn-content, pH-value and texture might be responsible for this strong Zn release. Moreover, Calmano et al. (2005) found a combination of several factors that lead to high dissolved amounts of TMs. They strongly suggested that the characterisation of the buffer capacity of investigated soils is essential for practical implementations, since it is assumed that periodical redox changes strongly affect low buffered sediments, because during oxidation buffering substances are consumed and displaced, respectively. This could be substantiated by our results. Dissolved concentrations of Cd, Cr, Ni, and Zn increased steadily within LS during the experiment and remained even in a solution by the end of the experiment. This can be explained by the soil characteristic that is dominated by sands, a very low pH-value, and thus an estimated low buffer capacity (see Table 4.1). The very low pH-value seemed to be mainly responsible for this behaviour. Calmano et al. (1993) demonstrated that after successive oxidation-reduction cycles, metal bindings changed from sulfide or organically bound to more labile phases due to a significant decrease in pH-value. On the contrary, the DS are dominated by clay and silt, high pH-values and thus an estimated high buffer capacity. Therefore, even though this soil showed the highest total pollution levels, most of the dissolved TMs (Cd, Cu, Cr, Zn) reached a maximum value but then decreased again. Consequently, at the end of the experiment only very slightly increased dissolved concentrations were identified compared to the beginning. In terms of these soil characteristics and TM pollution the PS can be settled between LS and DS. The soil proved to be a mixture of clay, silt and sand, with pH-values ranging from 4.9 to 6.7 and thus buffer capacities were estimated as moderate. This might be one reason why As, Cd, Cu, Cr, Ni reach a maximum value and then slightly increase (Ni, Cu) or remain constant (Cd, Cr). Zinc decreases constantly throughout the whole experiment. These findings tie in with the relative mobility introduced by Korte et al. (1976) and further adopted by Adriano (1986).

### 4.4.3 Explaining the variation of TM dissolution depending on wet-dry cycles

Climate change might affect water quality issues in rivers and lakes, but describing such effects is still at the very beginning (Delpla et al. 2009). Moreover, in floodplains only little is known about physic-chemical and biogeochemical conditions and processes causing the retention or the release of TMs. Additionally, only a few studies are available that discuss a combined effect of several soil parameters on TM release (Tiktak et al. 1998, Sauve et al. 2000, Smolders et al. 2009) or consider strong fluctuating hydrological conditions (Calmano et al. 2005, Hartley & Dickinson 2010).

Buchter et al. (1989) measured the so-called *Freundlich* parameters for 11 different soils and 15 TMs and identified pH-value, cation exchange capacity (CEC), and Fe/Al oxides as the most influential in terms of the dissolution of TMs. Moreover, they found significant relationships between soil properties and retention parameters in a group of highly diverse soils. The results of the GAM here partly confirm these outcomes. Models that included pH-values instead of $E_H$ were slightly better as also found by Grybos et al. (2007). Moreover Fe and S also contributed significantly to TM dissolution in all models that combine highly diverse soils. The importance of these two parameters has already been examined by several authors (e.g. Van Griethuysen 2006, Tack et al. 2006, Du Laing et al. 2007, Grybos et al. 2007). However, the results here make it also obvious that in nearly all cases several explanatory variables significantly determined TM release, leading to the assumption that a followed up investigation to interpret the explanatory variables for each soil independently is essential. The Pearson correlation coefficients for the explanatory variables for each soil individually demonstrate relations between the used explanatory variables. It became clear that combining very diverse soils for one analysis could mask the effects of some influential explanatory variables. This was particularly evident in the depression where DOC seemed to play a much more important role than shown by the GAM. The Pearson correlation coefficient is high between $E_H$ and DOC indicating that the simulation experiment has a strong influence on the DOC amount within the soil suspension during the experiment. ($E_H$: DOC= -0.85, $P<0.001$). This again leads to the assumption that the dissolution of some TMs should also be affected by fluctuating DOC amounts since it is known that OM in general is important in controlling metal mobility in wetland soils (e.g. Grybos et al. 2007, Schulz-Zunkel and Krueger 2009). However, assumptions that can be made from such correlations are not robust enough to relate them to the fate of TMs. However, because the dataset is relatively small (n=27 for each soil), fitting single models for each soil type and each TM is rather complicated because only a maximum of two explanatory variables could be included.

## 4.5 Conclusion

With this experiment we were able to identify TM release patterns for the three hydro-geomorphologic units: levee, depression, plateau, that is typical for these ecosystems. First, we found general trends in TM release, e.g. the low concentrations of Zn and Cd in anoxic phases; additionally we identified release patterns of TMs from floodplain soils. Thus we can state that one can assume high and more important continuous mobile amounts of TMs within the levee, which contrary is not a pollution hot spot referring to total TM concentrations. However, dissolved trace metal concentrations exceeded the critical values of the BBodSchV (1999) concerning the transfer pathway soil to groundwater, what emphasises the source function for pollutants of contaminated floodplain soils, for all plots.

Although the highest maximum dissolved concentrations were found within the levee (Cr, Ni, Zn) and the depression (As, Cd, Cu). Nevertheless, there are still several uncertainties that are mainly related to the strong spatial heterogeneity in floodplains as well as to temporal relationships and manifold interactions between biogeochemical factors and processes in soils. Thus, we can postulate that successive wet-dry cycles, which are common in floodplains, might always be auto-correlated. That means that the relations found in soils are dependent on what happened in a defined time prior to or following the investigation. Such coherences make it very complex and difficult to interpret and relate biogeochemical processes to TM release in soils. In the case of high buffered soils (e.g. DS) released amounts of e.g. Cd during dry phases can be rebound more quickly again during a following wet phase and thus mobile concentrations can be maintained nearly constant during wet-dry cycles. In a medium buffered soil (e.g. PS) dissolved Cd concentrations reach a maximum value but do not increase further or only very slightly above that maximum amount. However, in very low buffered soils (e.g. LS) mobile Cd concentrations increase steadily during the course of the experiment, irrespective of whether dissolved concentrations decreased throughout phases of low $E_H$ during the successive wet-dry cycle. This emphasised that total TM concentrations alone were a poor predictor of toxicity in soils since from non-pollution hot spots (like the LS) high amounts of retained TMs can be released under certain circumstances. Particularly with view to the combined effects of several soil parameters on TM release from floodplain soils, further detailed research including the speciation of metals and most probably long-term monitoring is required, especially against the background of adaptation and mitigation strategies for climate change. It is known that the adaptive capacity of natural ecosystems with respect to climate change is limited by the exposure and sensitivity to non-climatic threats. Especially when considering possible feedback loops that may amplify human effects, and are likely to increase the effects of synergies among multiple stressors. Overall it is important to consider the characteristics of the whole catchment area when implementing floodplain management activities since esp. spatial as well as temporal uncertainties may exist. In particular, since our findings suggest that a release of the investigated TMs can happen, using metal-enriched soils that are exposed to flooded-dried conditions potential environmental risks might be created.

Acknowledgements

This paper has been written with data collected during the EU-project Eurolimpacs (EU Contract no. GOCE-CT-2003-505540). We thank Sarah Gwillym-Margianto, as a native speaker, for proofreading the manuscript.

## References

Adams, M.S., Ballin, U., Gaumert, T., Hale, B.W., Kausch, H., Kruse, R., 2001. Monitoring selected indicators of ecological change in the Elbe River since the fall of the Iron Curtain. Environmental Conservation 28:333-344.

Adriano, D.C., 1986. Trace elements in the terrestrial environment. Springer, New York.

AG Boden, 2005. Bodenkundliche Kartieranleitung (KA5). Hannover.

BBodSchV, 1999. BGBl. I S. 1554, Stand: Geändert durch Art. 2 V v. 23.12.2004 I 3758.

Buchter, B., Davidoff, B., Amacher, M.C., Hinz, C., Iskandar, I.K., Selim, H.M., 1989. Correlation of Freundlich kd and n retention parameters wit h soils and elements. Soil Science 148:370-379.

Calmano, W., Hong, J., Forstner, U., 1993. Binding and mobilization of heavy metals in contaminated sediments affected by pH and redox potential. Water Science and Technology 28:223-235.

Calmano, W., von der Kammer, F., Schwartz, R., 2005. Characterization of redox conditions in soils and sediments: Heavy metals., London, UK.

Capon, S.J., Chambers, L.E., Mac Nally, R., Naiman, R.J., Davies, P., Marshall, N., Pittock, J., Reid, M., Capon, T., Douglas, M., Catford, J., Baldwin, D.S., Stewardson, M., Roberts, J., Parsons, M., Williams, S.E., 2013. Riparian Ecosystems in the 21st Century: Hotspots for Climate Change Adaptation? Ecosystems 16:359-381.

Delpla, I., Jung, A.V., Baures, E., Clement, M., Thomas, O., 2009. Impacts of climate change on surface water quality in relation to drinking water production. Environment International 35:1225-1233.

Du Laing, G., Rinklebe, J., Vandecasteele, B., Meers, E., Tack, F.M.G., 2009. Trace metal behaviour in estuarine and riverine floodplain soils and sediments: A review. Science of the Total Environment 407:3972-3985.

Du Laing, G., Vanthuyne, D.R.J., Vandecasteele, B., Tack, F.M.G., Verloo, M.G., 2007. Influence of hydrological regime on pore water metal concentrations in a contaminated sediment-derived soil. Environmental Pollution 147:615-625.

EEA, 2012. Climate change, impacts and vulnerability in Europe 2012. An indicator-based report, Copenhagen.

Eisenmann, V., 2002. Die Bedeutung der Böden für das Renaturierungspotential von Rückdeichungsgebieten an der mittleren Elbe, Hamburger Bodenkundliche Arbeiten, 51, PhD.

Frohne, T., Rinklebe, J., Diaz-Bone, R.A., Du Laing, G., 2011. Controlled variation of redox conditions in a floodplain soil: Impact on metal mobilization and biomethylation of arsenic and antimony. Geoderma 160: 414-424.

Frohne, T., Rinklebe, J., Langer, U., Du Laing, G., Mothes, S., Wennrich, R., 2012. Biogeochemical factors affecting mercury methylation rate in two contaminated floodplain soils. Biogeosciences 9:493-507.

Grybos, M., Davranche, M., Gruau, G., Petitjean, P., 2007. Is trace metal release in wetland soils controlled by organic matter mobility or Fe-oxyhydroxides reduction? Journal of Colloid and Interface Science 314:490-501.

Hartley, W., Dickinson, N.M., 2010. Exposure of an anoxic and contaminated canal sediment: Mobility of metal(loid)s. Environmental Pollution 158:649-657.

Heinrich, K., Rinklebe, J., Neue, H.U., 2000. Einfluß des heißwasserlöslichen Kohelnstoffs auf Redoxpotentialänderungen während simulierter Hochwasserereignisse in Auenböden. pp. 47-54. In: K. Friese, B. Witter, G. Miehlich, M. Rode (eds.) Stoffhaushalt von Auenökosystemen – Böden, Hydrologie, Schadstoffe, Bewertungen. Springer, Berlin, Heidelberg.

IUSS/ISRIC/FAO, 2006. World reference base for soil resources, Rome.

Joubert, A., Lucas, L., Garrido, F., Joulian, C., Jauzein, M., 2007. Effect of temperature, gas phase composition, pH and microbial activity on As, Zn, Pb and Cd mobility in selected soils in the Ebro and Meuse Basins in the context of global change. Environmental Pollution 148:749-758.

Körschens, M., Schulz, E., Klimanek, E.-M., Franko, U., 1990. Die organische Bodensubstanz-Bedeutung, Definition,Bestimmung. Archiv für Acker- und Pflanzenbau und Bodenkunde 41:427-434.

Korte, N.E., Skopp, J., Fuller, W.H., Niebla, E.E., Aleshii, B.A., 1976. Trace element movement in soils: influence of soil physical and chemical properties. Soil Science 122:350-359.

Krueger, F., Groengroeft, A., Grunewald, K., Meissner, R., Petzoldt, H., Schwartz, R., 2004. Pollution of Elbe River floodplains and consequences for future research 11th Magdeburg Seminar on Waters in Central and Eastern Europe. Assessment, Protection, Management, Leipzig.

Lair, G.J., Graf, M., Zehetner, F., Gerzabek, M.H., 2008. Distribution of cadmium among geochemical fractions in floodplain soils of progressing development. Environmental Pollution 156:207-214.

Lair, G.J., Zehetner, F., Fiebig, M., Gerzabek, M.H., Van Gestel, C.A.M., Hein, T., Hohensinner, S., Hsu, P., Jones, K.C., Jordan, G., Koelmans, A.A., Poot, A., Slijkerman, D.M.E., Totsche, K.U., Bondar-Kunze, E., Barth, J.A.C., 2009. How do long-term development and periodical changes of river-floodplain systems affect the fate of contaminants? Results from European rivers. Environmental Pollution 157:3336-3346.

Maes, J., Hauck, J., Paracchini, M.L., Ratamäki, O., Termansen, M., Perez-Soba, M., Kopperoinen, L., Rankinen, K., Schägner, J.P., Peter Henrys, Cisowska, I., Zandersen, M., Jax, K., Notte, A.L., Leikola, N., Pouta, E., Smart, S., Berit Hasler, Lankia, T., Andersen, H.E., Carlo Lavalle, Vermaas, T., Alemu, M.H., Scholefield, P., Batista, F., Pywell, R., Hutchins, M., Blemmer, M., Fonnesbech-Wulff, A., Vanbergen, A.J., Münier, B., Baranzelli, C., Roy, D., Thieu, V., Zulian, G., Kuussaari, M., Thodsen, H., Alanen, E.-L., Egoh, B., Sørensen, P.B., Braat, L., Bidoglio, G., 2012. A spatial assessment of ecosystem services in Europe: methods, case studies and policy analysis - phase 2. Synthesis report., Partnership for European Environmental Research Ispra.

Patrick, J.W.H., Williams, B.G., Moraghan, J.T., 1973. A simple system for controlling redox potential and pH in soil suspensions. Soil Science Society of America Proceedings 37:331–332.

Petersen, W., Willer, E., Willamowski, C., 1997. Remobilization of trace elements from polluted anoxic sediments after resuspension in oxic water. Water, Air and Soil Pollution 99:515-522.

Poot, A., Gillissen, F., Koelmans, A.A., 2007. Effects of flow regime and flooding on heavy metal availability in sediment and soil of a dynamic river system. Environmental Pollution 148:779-787.

R Development Core Team, 2011. R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria3-900051-07-0 (URL http:// www.R-project.org/).

Rinklebe, J., 2004. Differenzierung von Auenböden der Mittleren Elbe und Quantifizierung des Einflusses von deren Bodenkennwerten auf die mikrobielle Biomasse und die Bodenenzymaktivitäten von β-Glucosidase, Protease und alkalischer Phosphatase, Martin-Luther-Universität Halle-Wittenberg, Halle, PhD.

Rinklebe, J., Du Laing, G., 2011. Factors controlling the dynamics of trace metals in frequently flooded soils. In: H.M. Selim, 2011.Dynamics and Bioavailability of Heavy Metals in the Root Zone, pp. 245-270, CRC Press. Taylor & Francis Group.

Rinklebe, J., During, A., Overesch, M., Du Laing, G., Wennrich, R., Stark, H.J., Mothes, S., 2010. Dynamics of mercury fluxes and their controlling factors in large Hg-polluted floodplain areas. Environmental Pollution 158:308-318.

Rinklebe, J., Franke, C., Neue, H.U., 2007. Aggregation of floodplain soils based on classification principles to predict concentrations of nutrients and pollutants. Geoderma 141:210-223.

Rinklebe, J., Heinrich, K., Neue, H.-U., 2001. Der umsetzbare Kohlenstoff als Indikator für die potentuielle bodenmirkobielle Aktivität in Auenböden, Leipzig.

Rinklebe, J., Langer, U., 2006. Microbial diversity in three floodplain soils at the Elbe River (Germany). Soil Biology and Biochemistry 38:2144-2151.

Rupp, H., Rinklebe, J., Bolze, S., Meissner, R., 2010. A scale-dependent approach to study pollution control processes in wetland soils using three different techniques. Ecological Engineering 36:1439-1447.

Salomons, W., 1998. Biogeodynamics of contaminated sediments and soils: Perspectives for future research. Journal of Geochemical Exploration 62:37-40.

Sauve, S., Hendershot, W., Allen, H.E., 2000. Solid-solution partitioning of metals in contaminated soils: Dependence on pH, total metal burden, and organic matter. Environmental Science and Technology 34:1125-1131.

Schlichting, E., Blume, H.-P., Stahr, K., 1995. Bodenkundliches Praktikum. Blackwell, Berlin. Blackwell, Berlin.

Scholten, M., Anlauf, A., Buechele, B., Faulhaber, P., Henle, K., Kofalk, S., Leyer, I., Meyerhoff, J., Purps, J., Rast, G., Scholz, M., 2005. The Elbe River in Germany—present state, conflicting goals, and perspectives of rehabilitation. Large Rivers 15:579–602.

Schulz-Zunkel, C., Krueger, F., 2009. Trace Metal Dynamics in Floodplain Soils of the River Elbe: A Review. Journal of Environmental Quality 38:1349-1362.

Schulz-Zunkel, C., Krueger, F., Rupp, H., Meissner, R., Gruber, B., Gerisch, M., Bork, H.-R., 2013. Spatial and seasonal distribution of tracemetals in floodplain soils. A case study with the Middle Elbe River, Germany. Geoderma 211–212:128–137.

Schwartz, R., 2001. Die Böden der Elbaue bei Lenzen und ihre möglichen Veränderungen nach Rückdeichung. Hamburger Bodenkundliche Arbeiten. 48, Ph.D.

Smolders, E., Oorts, K., Van Sprang, P., Schoeters, I., Janssen, C.R., McGrath, S.P., McLaughlin, M.J., 2009. Toxicity of trace metals in soils as affected by soil type and aging after contamination: using calibrated bioavailability models to set ecological soil standards. Environmental Toxicology and Chemistry 28:1633-1642.

Tack, F.M.G., Van Ranst, E., Lievens, C., Vandenberghe, R.E., 2006. Soil solution Cd, Cu and Zn concentrations as affected by short-time drying or wetting: The role of hydrous oxides of Fe and Mn. Geoderma 137:83-89.
Thonon, I., 2006. Deposition of sediment and associated heavy metals on floodplains. Utrecht Univerisity. Netherlands Geographical Studies 337, Ph.D.
Tiktak, A., Alkemade, J.R.M., Van Grinsven, J.J.M., Makaske, G.B., 1998. Modelling cadmium accumulation at a regional scale in the Netherlands. Nutrient Cycling in Agroecosystems 50:209-222.
Tockner, K., Lorang, M.S., Stanford, J.A., 2010. River Flood Plains Are Model Ecosystems to Test General Hydrogeomorphic and Ecological Concepts. River Research and Applications 26:76-86.
Van Griethuysen, C., de Lange, H.J., Van den Heuij, M., de Bles, S.C., Gillissen, F., Koelmans, A.A., 2006. Temporal dynamics of AVS and SEM in sediment of shallow freshwater floodplain lakes. Applied Geochemistry 21:632-642.
Yu, K.W., Bohme, F., Rinklebe, J., Neue, H.U., DeLaune, R.D., 2007. Major biogeochemical processes in soils - A microcosm incubation from reducing to oxidizing conditions. Soil Science Society of America Journal 71:1406-1417.
Yu, K.W., Rinklebe, J., 2011. Advancement in soil microcosm apparatus for biogeochemical research. Ecological Engineering 37:2071-2075.
Zuur, A., Ieno, E., Walker, N., Saveliev, A., Smith, G., 2009. Mixed effects Models and Extensions in ecology with R. Statistics for Biology and Health. Springer, New York.
Zuur, A.F., Ieno, E.N., Elphick, C.S., 2010. A protocol for data exploration to avoid common statistical problems. Methods in Ecology and Evolution 1:3-14.

## Appendix A

Summary statistics for the best fitted GAMs for TM dissolution during the simulated wet-dry cycles

*(exp.var=explaining variable, D.E. = deviance explained, Total df= total degrees of freedom, AIC=Akaike's Information Criterion)*

| exp. var. | F-value | P-value | Model performance | | | |
|---|---|---|---|---|---|---|
| | | | D.E. | Total df | AIC | n |
| **As**$_{EH}$ | | | 99.5 | 35.8 | 673 | 79 |
| fplot | 96.1 | <0.001 | | | | |
| $E_H$ | 9.72 | <0.001 | | | | |
| DOC | 3.86 | <0.001 | | | | |
| Fe | 30.67 | <0.001 | | | | |
| S | 5.67 | <0.001 | | | | |
| NO3 | 2.31 | 0.074 | | | | |
| fPN | 6.14 | <0.001 | | | | |
| **As**$_{pH}$ | | | 99.5 | 32.3 | 664 | 79 |
| fplot | 128.8 | <0.001 | | | | |
| pH | 9.01 | <0.001 | | | | |
| Fe | 51.67 | <0.001 | | | | |
| S | 10.93 | <0.001 | | | | |
| fPN | 29.29 | <0.001 | | | | |
| **Cd**$_{pH}$ | | | 92.6 | 29.11 | | 79 |
| fplot | 14.85 | <0.01 | | | | |
| pH | 6.14 | <0.05 | | | | |
| Fe | 5.69 | <0.001 | | | | |
| Mn | 3.55 | <0.001 | | | | |
| S | 2.99 | <0.01 | | | | |
| fPN | 2.46 | 0.57 | | | | |
| **Cu**$_{pH}$ | | | 86.5 | 25.86 | | 79 |
| fplot | 1.07 | 0.349 | | | | |
| pH | 5.57 | <0.001 | | | | |
| Fe | 11.2 | <0.01 | | | | |
| Mn | 2.74 | <0.1 | | | | |
| S | 4.66 | <0.001 | | | | |
| fPN | 5.67 | <0.001 | | | | |
| **Cr**$_{EH/pH}$ | | | 97.6 | 32.55 | | 79 |
| fplot | 0.31 | 0.739 | | | | |
| Fe | 11.38 | <0.001 | | | | |
| Mn | 3.34 | <0.01 | | | | |
| S | 5.16 | <0.001 | | | | |
| $NO_3$ | 3.38 | <0.1 | | | | |
| fPN | 5.16 | <0.001 | | | | |
| **Ni**$_{EH}$ | | | 96.5 | 32.09 | 601 | 79 |
| fplot | 11.6 | <0.001 | | | | |
| Fe | 6.78 | <0.001 | | | | |
| Mn | 10.57 | <0.001 | | | | |
| S | 5.13 | <0.001 | | | | |
| fPN | 4.22 | <0.001 | | | | |
| **Ni**$_{pH}$ | | | 97.7 | 36.47 | 578 | 79 |
| fplot | 7.00 | <0.01 | | | | |
| pH | 5.19 | <0.01 | | | | |
| DOC | 2.71 | <0.05 | | | | |
| Fe | 4.43 | <0.001 | | | | |
| Mn | 12.81 | <0.001 | | | | |
| S | 5.89 | <0.001 | | | | |
| fPN | 3.88 | <0.01 | | | | |
| **Zn**$_{EH}$ | | | 90.2 | 23.77 | 853 | 79 |
| fplot | 0.48 | 0.621 | | | | |
| $E_H$ | 10.02 | <0.001 | | | | |
| Fe | 4.84 | <0.05 | | | | |
| Mn | 17.69 | <0.001 | | | | |
| S | 9.47 | <0.001 | | | | |
| **Zn**$_{pH}$ | | | 93.8 | 34.37 | 838 | 79 |
| fplot | 4.57 | <0.05 | | | | |
| pH | 1.92 | <0.1 | | | | |
| Fe | 7.98 | <0.01 | | | | |
| Mn | 8.48 | <0.001 | | | | |
| S | 5.81 | <0.001 | | | | |
| fPN | 5.91 | <0.001 | | | | |

# Chapter 5

## Synopsis

## 5.1 Introduction

Since river-floodplain ecosystems are threatened by multiple stressors, the loss of these ecosystems still continues as does the loss of a multitude of ecosystem functions and services that are of great economic value to society (Oppermann et al. 2010). Some major threats to riparian ecosystems around the world include altered hydrological regimes due to river regulation and water extraction, the clearance of vegetation for agriculture and other developments, livestock grazing, the development of human settlements and infrastructure, pollution and mining (Tockner and Stanford 2002, Naiman et al. 2005). Global climate change is another threat that could impact river-floodplain ecosystems that are very vulnerable in this respect (Erwin 2009, Capon et al. 2013). To preserve river-floodplain ecosystems and their ecosystem functions and services, not only re-vitalisation measures but also sustainable management strategies as well as approaches for climate change adaptation and mitigation are absolutely imperative. This thesis aims to extend the existing knowledge on how river-floodplain ecosystems may be impacted by trace metal pollution and also covers aspects of climate change scenarios in floodplains, especially about the possibility that floodplain soils may shift from sinks to sources of potentially harmful solutes. For this, a floodplain segment along the lower Middle Elbe River was used as a model region. With a literature review on trace metal dynamics in floodplain soils, field measurements conducted over a three-year period to cope with seasonal changes in trace metal dynamics and a laboratory analysis to simulate a climate change scenario referring to stronger fluctuation between anaerobic and aerobic conditions in soils and related trace metal dynamics, the thesis covers several aspects of the recent discussion on this topic.

## 5.2 Key Findings

### 5.2.1 Key finding 1

**The quantification of metal mobilisation on the basis of changing physico-chemical and biogeochemical conditions, including changes from climate change, is still lacking**

Riverine floodplains are characterised by a high degree of variability in the frequency and the period of inundation of various morphological forms (Baldwin and Mitchell 2000). Deposited trace metal concentrations vary in space; greatest amounts of metals accumulate near to the natural levee, and in low-lying areas that are frequently inundated and in those places where large amounts of fine sediments are deposited (Middelkoop 2000, Krueger et al. 2005). Floodplains show a high variability of diffuse soil contamination where low pollutant concentrations can be found only a short distance from sites with high contamination (Kooistra et al. 2001). Due to long periods of contamination, sediments along European lowland rivers still show high levels of contamination (Van der Veen et al. 2006). Organic matter, clay minerals, and hydrous oxides behave as sinks for trace metals in floodplain soils. However, the combined effects of several soil parameters on trace metal release are still uncertain and more complicated to interpret, especially when considering field data. Moreover, it became clear that mobile resp. dissolved trace metal amounts within the soil solution or resp. in the soil suspension do not indicate the amount at which those concentrations may involve an eco-toxicological risk. For this, it is crucial to know the extent to which dissolved amounts of trace metals will be transported to water bodies or to plants. Interpreting this information is rather difficult because of the complex determination of transfer and translocation processes of trace metals through floodplain soils primarily due to a high spatial variability of soil conditions, trace metal contamination, and the mobility of trace metals in soils, as well as of plant community compositions. Moreover, groundwater recharge, the capillary ascent and evapotranspiration as well as changes to the storage function of the soils all need to be considered as part of the soil-water balance. In spite of this knowledge, a separation of the soil solution is not possible and thus the transport of mobile pollutants through the soil solution to other water bodies can still not be quantified to date. Thus it is still advisable to combine different measurement systems, such as field and laboratory investigations, to quantify mobile trace metals and also to count the transported amount of such pollutants through floodplain soils. Moreover, it is essential to understand the dynamics of sediment transport in the system including the sources, pathways and in-between storage of sediments for monitoring sediment-bound trace metals.

### 5.2.2 Key finding 2

**In floodplains, increased amounts of several dissolved trace metals can be found during as well as some time after flood events, also in areas not showing noticeable total trace metal concentrations.**

With the field investigations it was possible to allocate site characteristics with total as well as dissolved trace metal contents. We found seasonally-driven biogeochemical hot spots within the plot that showed highest total trace metal pollution levels, which additionally were very profound because of the great extremes. But even within the less polluted plot we found such hot spots. Furthermore, partially higher trace metal amounts with increasing soil depth in these two plots suggest a possible translocation of trace metals from the upper to the lower horizons. In terms of the soil parameters that may influence trace metal mobility we were able to conclude that the redox potential may serve as a predictor for trace metal dissolution in floodplain soils, at least for two of the three investigated plots. Apart from that we identified seasonal changes in trace metal dissolution related to the course of the redox potential enabling a distinction between the behaviour of the investigated trace metals. These two plots are also in the focus with respect to identifying hot moments leading to small-scale hot spots.

For Cu and Cr we identified such hot spots during late summer and early autumn in the less-polluted plot, which confirms that these two metals are remobilised during periods of high redox potential. Conversely, this will apply to Ni and Zn in this plot; hot spots seem to be delayed following usual flood events as we found minimum dissolved concentrations of Ni and Zn with increasing redox potential in soils. The most polluted plot showed one strong hot spot of increased amounts of dissolved As that also coincided with a hot moment which in this case is during a typical flood event in spring. Both are found within the lowest investigated horizon and therefore might also indicate the transport of trace metals through percolating water.

### 5.2.3 Key finding 3

**Plot-specific trace metal release patterns could be identified. However, there are still uncertainties concerning the combined effects of several soil parameters on trace metal release.**

In the laboratory investigations we could clearly identify different trace metal release patterns for every plot investigated. The release patterns are highly related to the buffer capacity of the soils investigated. Within the levee that is dominated by sand with a very low pH-value, dissolved concentrations of Cd, Cr, Ni, and Zn increased steadily during the experiment and remained at a constant level in the solution by the end of the experiment. Contrarily, in the depression dominated by clay and silt with high pH-values and thus assumingly a high buffer capacity but also with the highest total pollution levels, dissolved Cd, Cu, Cr and Zn reached maximum values but then decreased again. By the end of the experiment only slightly increased dissolved concentrations were identified compared to the beginning. Within the plateau that showed a mixture of clay, silt and sand, pH-values from 4.9 to 6.7 and thus moderate buffer capacities, dissolved amounts of As, Cd, Cu, Cr, and Ni also reached a peak value after which only Ni and Cu slightly increased and Cd, Cr remained constant. Zn decreases constantly throughout the entire experiment. From that we were able to conclude that the characterisation of the buffer capacity of the investigated soils is essential for practical implementations, since it is assumed that periodical redox changes strongly affect low-buffered sediments, because during oxidation buffering substances are consumed and displaced, respectively. However, it could not significantly distinguished between which soil parameters those release patterns could be assigned to. Nearly all soil parameters that were tested contributed significantly to the explanation of the trace metal deviance during the experiment. Only Fe and S could be identified as significant for explaining all trace metal dynamics in all soils.

## 5.3 Concluding remarks

The results of this thesis strongly confirm that two main key characteristics of (mostly undisturbed) riparian ecosystems are crucial for ecosystem functioning in floodplains: high spatial connectivity (internally and in relation to adjacent ecosystems) and high levels of environmental heterogeneity (Capon et al. 2013). If these key parameters are given, floodplains are usually able to improve river as well groundwater quality. However, due to this connectivity between floodplains and their adjacent rivers, remnants of the existing undisturbed floodplains are heavily loaded with several pollutants, including trace metals. Total but also dissolved trace metal concentrations in floodplain soils often meet the given threshold values according to existing regulations such as the German Soil Protection Guideline (BBodSchV 1999); the latter in particular need to be considered seriously in terms of ecotoxicology as floodplains react very sensitively to matter mobilisation and accumulation (Merz et al. 2009). Additionally, trace metal bioavailability is not a constant factor and may fluctuate in time but also in space; vertically and horizontally within a floodplain. At the same, the time effects of climate change such as changes to riparian vegetation that may alter the input of sediments and pollutants (e.g. Davies 2010) or changes to fluvial regimes that lead to a changing physical, chemical, and biological heterogeneity of riparian ecosystems (Capon et al. 2013) make general advice on the management of polluted floodplains very complicated.

The results of this thesis highlight the fact that although knowledge exists in this field, there are still many knowledge gaps to be filled. The review in chapter two emphasized these knowledge gaps and illustrated the problem that bundles of biogeochemical processes that are difficult to separate are relevant for trace metal dynamics in floodplain soils. Moreover, the identified lack of existing general advices regarding floodplain management activities led to a selection of the studied plots that are generally typical for floodplains. With this selection, a transformation of the results to larger scales may be possible in the future. The research questions in Chapter three and four were based on the general existing uncertainties about bioavailaibility in floodplain soils. The combination of field and laboratory investigations were complementary as it made clear that results from the laboratory can rarely be transformed to the field and vice versa.

Nevertheless, the field investigations showed that plot-specific very detailed information can be collected on trace metal dynamics and their relations to hydrology, topography, soil parameters etc. This can be very helpful in terms of small-scale and short-term floodplain management such as providing consultation on uses compatible with the results from Groengroeft et al. (2005) who stated for example that particularly after flood events grazing should be discontinued in floodplains. Additionally, Overesch et al. (2007) indicated that especially flood channels and depressions revealing the highest total contamination and/or phytoavailability should be precluded from grazing and instead only used for mown grass, since grazing animals may also take up significant amounts of trace metals from the inhalation and ingestion of contaminated soils (Thornton and Abrahams 1983). With the results of the thesis it should be added that floodplain areas as a whole, including levees that are non-total pollution hot spots, must be considered for management actions especially against the background of possible transfer processes that involve the transport of mobile trace metals into food chains, and to ground- and surface waters.

The laboratory experiment revealed the very complex coherences between dissolved trace metals and biogeochemical processes in soils. Even if it was possible to identify trace metal release patterns per plot we can say very little about which soil parameters could be directly or indirectly affected by the simulated wet-dry cycles. Therefore, coherences between biogeochemistry and trace metal release still remain unclear. Consequently, further research (particularly in the face of climate change) but also long-term and more detailed experiments are necessary in the future.

Bringing those outcomes together it has to be reflected that the adaptability of natural ecosystems with respect to climate change is limited by the exposure and sensitivity to non-climatic threats. This is particularly true when considering that possible feedback loops might amplify anthropogenic effects on e.g. riparian ecological dynamics more rapidly in the future, and are likely to increase the effects of synergies among multiple stressors (Capon et al. 2013). Such coherences between anthropogenic threats and climate change in floodplains made interpretation and relating biogeochemical processes to trace metal release or retention in soils, again, very complex. In particular, the investigation and interpretation of the effects of a multitude of explanatory variables on trace metal bioavailability is extremely complicated. Thus, by putting the potentially adverse effects of trace metal pollution into a greater context, such as the concept of ecosystem functions and services, deeper knowledge about associated processes is required. For example Kools et al. (2008) found out that predicting the effects of pollution on ecosystem stability in general is not always straightforward. It is rather difficult to predict when and to what extent e.g. the bioavailability of metals, and thus an eco-toxicological risk, will increase, and whether this will lead to trace metal transfer in ground- and surface waters and to a possible uptake in food chains. More generally, it is specified that polluted soils showed lower bacterial growth, decreased soil faunistic biomass and diversity as well as more nitrate leaching (Kools et al. 2008). As the effects of contaminants are highly confounded by other anthropogenic influences and naturally varying factors one needs to consider all possible stress factors other than contaminants and at the same time conduct an analysis of all relevant agents to put the effects of contamination into the right perspective (Van Straalen and Van Gestel 2008). In particular, diffuse pollution, e.g. from overbank flooding, and even low pollution levels can affect local ecosystems to different degrees as effects are not easily detected and local responses can differ considerably (Posthuma et al. 2008). The latter in particular requires ongoing site-specific assessments (see Braumann et al. 2007) as site characteristics also include total as well as dissolved trace metal contents. Van Griethuysen et al (2003) highlighted the fact that small-scale spatial variations are essential for addressing the risk assessment of trace metals. They found that e.g. common alternative sediment quality criteria like SEM-AVS (simultaneously extracted metals-acid-volatile sulfide) and total trace metal concentrations may lead to different priority settings for contaminated sites mainly due to variances in the spatial variability of the underlying variables. Even with almost constant metal or SEM concentrations, metal-associated risks may vary among sites because of spatial variation in environmental conditions such as redox potential and subsequently AVS. Moreover, very often hidden effects such as latent effects, ecological phenomena and multiple stressors (Posthuma et al. 2008) can make it extremely complicated to identify diffuse pollution.

Similar conclusions can also be drawn from the results obtained here; the field investigations very clearly showed highly heterogeneous total trace metal contents and also very diverse dissolved trace metal contents due to a very high spatial variation within the study area. The same could be said after interpreting the laboratory results; the three investigated soils responded very differently to the simulated wet-dry cycles in terms of changing soil parameters and also dissolved trace metals. Moreover, due to the uncertainties that still remain between biogeochemical processes and trace metal dynamics we assume difficulties in transferring the results obtained to larger scales or even to other river-floodplain ecosystems even if the selected study plots are typical geomorphological units in floodplains.

So, where should we go from here? Due to existing toxicological problems in floodplains, appropriate management actions to prevent trace metal mobilisation, an increase in bioavailability and an enhanced transfer of metals to the food web is urgently needed (Du Laing et al. 2007). However, long-term management strategies for floodplains that consider seasonal but also climate change as drivers for those processes cannot be clearly defined at the moment. Nevertheless, especially for those floodplains that are considered to play an important role in the development of sustainable water management strategies for the future (Merz et al. 2009) pollution and climate change issues have to be examined holistically, which is not that simple especially for managers.

Brauman et al. (2007) pointed out the tremendous potential for the concept of ecosystem functions and services for protecting floodplain ecosystems and their viability. The concept links conservation and development by, among others, relating environmental and human health. This can be extremely valuable especially in riparian ecosystems that provide a high diversity and value of functions, goods and services. At the same time they are traditionally under high anthropogenic use and pollution may affect those services to different extents. This comes more clearly by reflecting the aim of the Water Framework Directive (WFD) and its central question such as how a 'good ecological status' can practically be achieved locally not only for water, but also for sediment and soil, also considering the Soil Protection Guidelines (e.g. BBodSchV 1999) and the close interrelations between river water, ground water and floodplain soils.

Posthuma et al. (2008) strongly recommend that floodplains need a risk management where site managers will have to handle risks rather than effects as effect-oriented settings are always "too late", because action is only taken when effects become more visible. Moreover, science-based and practical methods are required that manage contaminated sites so that an optimum ecological status can be reached. This requires, for example, attention to the spatial and temporal aspects of contamination relating to the biological recovery potential of species. In fact, research on all "uncertainties" such as e.g. bioavailability is highly necessary. Posthuma et al. (2008) introduced a three-pronged approach. The first and fundamental goal is prevention (to avoid risks from arising), the second is management (to cope with situations of diffuse and serious pollution) and the third is ecological recovery.

Van Straalen and Van Gestel (2008) suggest using a multidimensional stress ecology framework as an appropriate assessment instrument to separate the effects of pollution from other anthropogenic disturbances and naturally variable factors. Because moderately low concentrations associated with diffuse pollution can cause effects that interact with natural stress factors; sensitive tools are needed to differentiate between the two.

Besides, awareness about the importance of floodplain restoration, including re-connecting floodplains to their adjacent rivers has significantly increased throughout Europe, as it is well known that many floodplains no longer fulfil their hydrological, biological and geochemical key functions (Fokkens 2008) and that adaptation to other anthropogenic threats as well as climate change is urgently needed. When one takes particular consideration of the multiple beneficial hydrological, ecological and socio-economic functions and values of river-floodplain ecosystems, one can easily see how floodplain restoration has become an important policy issue especially in terms of giving more space to rivers (Moss and Monstadt 2008). However, up until now there have only been realised a limited number of projects restoring functional floodplains in Europe (Ledoux 2005). This is partly due to human activities that are dominant in floodplains such as settlements, agricultural land use, flood defence etc. and the continual importance of those activities which are often contradictory to vital floodplain ecosystems. Moreover, floodplain re-vitalisation calls for complex institutional reforms in various policy and social fields, numerous stakeholders and interests need to be considered, laws and regulation requirements need to be met. Beyond that, hydrological, geomorphological but also biogeochemical issues need to be considered for successful ecological re-vitalisiation measures (Lamers et al. 2006). Thus characteristics of the entire catchment area need to be taken into reflection as spatial as well temporal uncertainties may exist. All of these aspects make floodplain re-vitalisation projects highly complex and often also unpredictable (cf. Moss and Monstadt 2008).

Overall, the dynamics of trace metal pollution in floodplains and its possible effects on ecosystem structure and functioning is very complex. Until now there is still no single answer how to maintain or enhance ecosystem functions and services of floodplains that are adversely affected by trace metal pollution. It is therefore imperative to continue research, especially in terms of identifying multiple factors that may affect trace metal dynamics. This as well potential relationships between anthropogenic threats and climate change in floodplain ecosystems needs to be seriously taken into thinking when planning future management activities where a detailed understanding of trace metal dynamics in floodplains is essential. What it is already widely recognised is the crucial need for sustainable floodplain management, primarily in terms of several ecosystem services such as flood protection and water quality measures but also as adaptation and mitigation measures concerning climate change. Additionally, further understanding of trace metal dynamics in re-vitalised floodplains focusing on water quality aspects in terms of the WFD and Soil Protection Guidelines is highly recommended.

As natural riverine floodplain ecosystems may already have a reasonably high capacity to adapt to various anthropogenic as well environmental changes because they have evolved under, and are structured by, relatively high environmental dynamics, it is highly advantageous to monitor those ecosystems continuously.

Figure 5.1 The Elbe flood in spring 2006 in the floodplain area ‘Schönberg Deich‘ (Source: C. Schulz-Zunkel)

## Bibliography


Adams, D.D., 1994. Sediment pore water sampling. pp. 171-202. In: A. Murdoch, S.D. MacKnight (eds.) Handbook of Techniques for Aquatic Sediments Sampling, Lewis, Boca Raton, FL.

Adams, M.S., Ballin, U., Gaumert, T., Hale, B.W., Kausch, H., Kruse, R., 2001. Monitoring selected indicators of ecological change in the Elbe River since the fall of the Iron Curtain. Environmental Conservation 28:333-344.

Adams, M.S., Kausch, H., Gaumert, T., Kruger, K.E., 1996. The effect of the reunification of Germany on the water chemistry and ecology of selected rivers. Environmental Conservation 23:35-43.

Adriano, D., 2001. Biogeochemical processes regulating metal behaviour. pp. 30-59. In: D. Adriano (ed.) Trace elements in terrestrial environments: Biogeochemistry, bioavailability and risks of metals. Springer, New York.

Adriano, D.C., 1986. Trace elements in the terrestrial environment. Springer, New York.

AG Boden, 2005. Bodenkundliche Kartieranleitung (KA5). Hannover.

Albering, H.J., Van Leusen, S.M., Moonen, E.J.C., Hoogewerff, J.A., Kleinjans, J.C.S., 1999. Human health risk assessment: A case study involving heavy metal soil contamination after the flooding of the river Meuse during the winter of 1993-1994. Environmental Health Perspectives 107:37-43.

Alloway, B.J., 1997. The mobilisation of trace elements in soils. Contaminated Soils, Paris (France), May 15-19, 133-145.

Amoros, C., Roux, A.L., 1988. Interaction between water bodies within the floodplains of large rivers: function and development of connectivity. Münstersche Geographische Arbeiten, pp. 125-130.

ARGE-Elbe (Arbeitsgemeinschaft zur Reinhaltung der Elbe), 1984–2000. Tables of monitoring measurements, Hamburg. *Available at www.arge-elbe.de/wge/Download/DDaten.php (verified 23 Mar. 2009).*

Baldwin, D.S., Mitchell, A.M., 2000. The effects of drying and re-flooding on the sediment and soil nutrient dynamics of lowland river-floodplain systems: A synthesis. Regulated Rivers, Research and Management 16:457-467.

Barona, A., Romero, F., 1997. Relationships among metals in the solid phase of soils and in wild plants. Water Air and Soil Pollution 95:59-74.

Bartlett, R., James, B., 1979. Behavior of chromium in soils: III Oxidation. Journal of Environmental Quality 8:31-36.

BBodSchV, 1999. BGBl. I S. 1554, Stand: Geändert durch Art. 2 V v. 23.12.2004 I 3758.

Bethge-Steffens, D., 2008. Der Bodenwasserhaushalt von zwei reprasentativen Flussauenstandorten der Mittelelbe, Untersuchungen mit wägbaren Grundwasserlysimetern, UFZ-Diss. 1/2008, Leipzig. PhD.

Berner, R.A., 1980. Early Diagenesis: A theoretical approach. Princton University Press, Princton, NJ.

BfG (Bundesanstalt für Gewässerkunde), 2002. Das Augusthochwasser 2002 im Elbegebiet, Koblenz.

Blume, H.P., Brummer, G., 1991. Prediction of heavy metal behavior in soil by means of simple field tests. Ecotoxicology and Environmental Safety 22:164-174.

Brack, W., Klamer, H.J.C., de Ada, M.L., Barcelo, D., 2007. Effect-directed analysis of key toxicants in European river basins - A review. Environmental Science and Pollution Research 14:30-38.

Brallier, S., Harrison, R.B., Henry, C.L., Dongsen, X., 1996. Liming effects on availability of Cd, Cu, Ni and Zn in a soil amended with sewage sludge 16 years previously. Water Air and Soil Pollution 86:195-206.

Brauman, K.A., Daily, G.C., Duarte, T.K., Mooney, H.A., 2007. The nature and value of ecosystem services: An overview highlighting hydrologic services. Annual Review of Environment and Resources:67-98.

Bruemmer, G.W., Gerth, J., Herms, U., 1986. Heavy metal specie, mobility and availability in soils. Zeitschrift für Pflanzenernährung und Bodenkunde 149:382-398.

Buchter, B., Davidoff, B., Amacher, M.C., Hinz, C., Iskandar, I.K., Selim, H.M., 1989. Correlation of Freundlich kd and n retention parameters wit h soils and elements. Soil Science 148:370-379.

Burton, G.A., 1992. Assessing contaminated aquatic sediments. Environmental Science and Technology 26:1862-1862.

Calmano, W., Hong, J., Forstner, U., 1993. Binding and mobilization of heavy-metals in contaminated sediments affected by pH and redox potential. Water Science and Technology 28:223–235.

Calmano, W., von der Kammer, F., Schwartz, R., 2005. Characterization of redox conditions in soils and sediments: Heavy metals. IWA Publication, London, UK

Capon, S.J., Chambers, L.E., Mac Nally, R., Naiman, R.J., Davies, P., Marshall, N., Pittock, J., Reid, M., Capon, T., Douglas, M., Catford, J., Baldwin, D.S., Stewardson, M., Roberts, J., Parsons, M., Williams, S.E., 2013.

Riparian Ecosystems in the 21st Century: Hotspots for Climate Change Adaptation? Ecosystems 16:359-381.
Charlatchka, R., Cambier, P., 2000. Influence of reducing conditions on solubility of trace metals in contaminated soils. Water Air and Soil Pollution 118:143-167.
Chuan, M.C., Shu, G.Y., Liu, J.C., 1996. Solubility of heavy metals in a contaminated soil: Effects of redox potential and pH. Water Air and Soil Pollution 90:543-556.
Ciszewski, D., Czajka, A., Blazej, S., 2008. Rapid migration of heavy metals and (137)Cs in alluvial sediments, Upper Odra River valley, Poland. Environmental Geology 55:1577-1586.
Commission, E., 2000. Directive 2000/60/EC of the European parliament and of the office council of 23. Oct 2000 establishing a framework for Community action in the field of water poilicy (Water Framework Directive. In: O.J.o.t.E. Communities (Ed.), L 327/1. Europena Commission, Brussels, pp. 72.
Costanza, R., dArge, R., de Groot, R., Farber, S., Grasso, M., Hannon, B., Limburg, K., Naeem, S., Oneill, R.V., Paruelo, J., Raskin, R.G., Sutton, P., Van den Belt, M., 1997. The value of the world's ecosystem services and natural capital. Nature 387:253-260.
Davies, B.E., 1992. Interrelationships between soil properties and the uptake of cadmium, copper, lead and zinc from contaminated soils by radish (Raphanus sativus L). Water Air and Soil Pollution 63:331–342.
Davies, P.M., 2010. Climate Change Implications for River Restoration in Global Biodiversity Hotspots. Restoration Ecology 18:261-268.
Davranche, M., Bollinger, J.C., 2000a. Heavy metals desorption from synthesized and natural iron and manganese oxyhydroxides: Effect of reductive conditions. Journal of Colloid and Interface Science 227:531-539.
Davranche, M., Bollinger, J.C., 2000b. Release of metals from iron oxyhydroxides under reductive conditions: Effect of metal/solid interactions. Journal of Colloid and Interface Science 232:165-173.
Delpla, I., Jung, A.V., Baures, E., Clement, M., Thomas, O., 2009. Impacts of climate change on surface water quality in relation to drinking water production. Environment International 35:1225-1233.
Dong, D.M., Yang, F., Yu, L., Hua, X.Y., Lu, X.J., Zhang, J.J., 2005. Adsorption of Pb, Cd to Fe, Mn oxides in natural freshwater surface coatings developed in different seasons. Journal Of Environmental Sciences-China 17:30-36.
Du Laing, G., Rinklebe, J., Vandecasteele, B., Meers, E., Tack, F.M.G., 2009. Trace metal behaviour in estuarine and riverine floodplain soils and sediments: A review. Science of the Total Environment 407:3972-3985.
Du Laing, G., Vanthuyne, D.R.J., Vandecasteele, B., Tack, F.M.G., Verloo, M.G., 2007. Influence of hydrological regime on pore water metal concentrations in a contaminated sediment-derived soil. Environmental Pollution 147:615-625.
Duft, M., Tillman, M., Oehlmann, J., 2003. Ökotoxikologische Sedimentkartierung der großen Flüsse Deutschlands, Berlin.
Duve, J., 1999. Bilanzierung des Stoffaustausches zwischen Elbe und Deichvorland am Beispiel zweier Tidebeeinflusster Untersuchungsgebiete. Hamburger Bodenkundliche Arbeiten, 43, PhD.
EEA, 1995. Europe's environment. The Dobris assessment, Copenhagen.
EEA, 2012. Climate change, impacts and vulnerability in Europe 2012. An indicator-based report, Copenhagen.
Eisenmann, V., 2002. Die Bedeutung der Böden fur das Renaturierungspotential von Rückdeichungsgebieten an der mittleren Elbe. Hamburger Bodenkundliche Arbeiten, 51, Ph.D.
Engel, H., 2004. The flood event 2002 in the Elbe river basin, causes of the flood, its course, statistical assessment and flood damages. Houille Blanche-Revue Internationale De L Eau 6:33–36.
Erwin, K.L., 2009. Wetlands and global climate change: the role of wetland restoration in a changing world. Wetlands Ecology and Management 17:71-84.
Fergusson, J.E., 1990. The heavy elements, chemistry, environmental impact and health effects. 1st ed. Pergamon Press, Oxford.
Fokkens, B., 2008. Foreword: European Centre for River Restoration. In: T. Moss, J. Monstadt (eds.) Restoring floodplains in Europe. IWA Publishing.
Foster, I.D.L., Charlesworth, S.M., 1996. Heavy metals in the hydrological cycle: Trends and explanation. Hydrological Processes 10:227-261.
Friese, K., 2006. Floodplains and areas of low water movement as the linking part in the transport of suspended particulate matter and sediments along lowland rivers. Acta Hydrochimica Et Hydrobiologica 34:171-173.

Frohne, T., Rinklebe, J., Diaz-Bone, R.A., Du Laing, G., 2011. Controlled variation of redox conditions in a floodplain soil: Impact on metal mobilization and biomethylation of arsenic and antimony. Geoderma 160:414-424.

Frohne, T., Rinklebe, J., Langer, U., Du Laing, G., Mothes, S., Wennrich, R., 2012. Biogeochemical factors affecting mercury methylation rate in two contaminated floodplain soils. Biogeosciences 9:493-507.

Gambrell, R.P., 1994. Trace and toxic metals in wetlands–A review. Journal of Environmental Quality 23:883–891.

Gambrell, R.P., Collard, V., Patrick, W. Jr., 1980. Cadmium uptake by marsh plants as aff ected by sediment physicochemical conditions. pp. 425–444. In: R.A. Baker (ed.) Contaminants and sediments, Ann Arbor Science.

Gambrell, R.P., DeLaune, R., Patrick, W. Jr., 1991a. Redox processes in soils following oxygen depleting. pp. 101–117. In: M.B. Jackson et al. (ed.) Plant life under oxygen deprivation. SpB Academic Publication, The Hague.

Gambrell, R.P., Patrick, W. Jr., 1988. The influence of redox potential on the environmental chemistry of contaminants in soils and sediments. pp. 319–333. In: D.D. Hook (ed.) The ecology and management of wetlands. Timber Press, Portland, OR.

Gambrell, R.P., Wiesepape, J.B., Patrick, W.H., Duff, M.C., 1991b. The effects of pH, redox, and salinity on metal release from a contaminated sediment. Water Air and Soil Pollution 57:359–367.

Geller, W., Ockenfeld, K., Böhme, M., Knöchel, A. (ed.), 2004. Schadstoffbelastung nach dem Elbe-Hochwasser 2002, Endbericht des Adhoc-Projekts: Schadstoffuntersuchungen nach dem Hochwasser vom August 2002, Ermittlung der Gefährdungspotentiale an Elbe und Mulde. BMBF Forderkennzeichen PTJ 0330492 KDD, Nürnberg.
*Available at http:// www.ufz.de/hochwasser/bericht/HWEnd.pdf (verified 25 Mar. 2009).*

Gibbard, P.L., Rose, J., Bridgland, D.R., 1988. The history of the great northwest European rivers during the past three million years. Philosophical Transactions of the Royal Society of London 318:559-602.

Graf, M., Lair, G.J., Zehetner, F., Gerzabek, M.H., 2007. Geochemical fractions of copper in soil chronosequences of selected European floodplains. Environmental Pollution 148:788-796.

Gregory, S.V., Swanson, F.J., McKee, W.A., Cummins, K.W., 1991. An ecosystem perspective of riparian zones. Bioscience 41:540-551.

Groengroeft, A., Kruger, F., Grunewald, K., Meissner, R., Miehlich, G., 2005. Plant and soil contamination with trace metals in the Elbe floodplains: A case study after the flood in August 2002. Acta Hydrochimica Et Hydrobiologica 33:466-474.

Grybos, M., Davranche, M., Gruau, G., Petitjean, P., 2007. Is trace metal release in wetland soils controlled by organic matter mobility or Fe-oxyhydroxides reduction? Journal of Colloid and Interface Science 314:490-501.

Hamilton-Taylor, J., Davison, W., 1995. Redox-driven cycling of trace elements in lakes. pp. 217-263. In: A. Lerman, D. Imboden, J. Gat (eds.) Physics and Chemistry of Lakes. Springer, Berlin.

Hansson, L.A., Bronmark, C., Nilsson, P.A., Abjornsson, K., 2005. Conflicting demands on wetland ecosystem services: nutrient retention, biodiversity or both? Freshwater Biol 50:705-714.

Harres, H.P., 1998. Schwermetallgehalte in Böden, Pflanzen, Fließgewässern und Sedimenten unterschiedlich belasteter Regionen Südsardiniens. Untersuchungen zur regionalen Differenzierung und zeitlichen Veränderung sowie zur geoökologischen Relevanz von Schwermetallverlagerungen. University of Halle/Saale, Habilitation.

Harter, R.D., Naidu, R., 2001. An assessment of environmental and solution parameter impact on trace-metal sorption by soils. Soil Science Society of America Journal 65:597-612.

Hartley, W., Dickinson, N.M., 2010. Exposure of an anoxic and contaminated canal sediment: Mobility of metal(loid)s. Environmental Pollution 158:649-657.

Heinrich, K., Rinklebe, J., Neue, H.U., 2000. Einfluß des heißwasserlöslichen Kohelnstoffs auf Redoxpotentialänderungen während simulierter Hochwasserereignisse in Auenböden. pp. 47-54. In: K. Friese, B. Witter, G. Miehlich, M. Rode (eds.) Stoffhaushalt von Auenökosystemen-Böden, Hydrologie, Schadstoffe, Bewertungen. Springer, Berlin, Heidelberg.

Herms, U., Brummer, G., 1984. Solubility and retention of heavy metals in soils. Zeitschrift für Pflanzenernährung und Bodenkunde 147:400-424.

Hobbelen, P.H.F., Koolhaas, J.E., Van Gestel, C.A.M., 2004. Risk assessment of heavy metal pollution for detritivores in floodplain soils in the Biesbosch, the Netherlands, taking bioavailability into account. Environmental Pollution 129:409-419.

Hoehn, A., Hierold, W., Preitzsch, C., Schalitz, G., 2000. Schwermetallverteilung in Auenböden des Nationalparks UNteres Odertal. pp. 359-368. In: K. Friese, B. Witter, G. Miehlich, M. Rode (eds.)

Stoffhaushalt von Auenökosystemen. Böden, Hydrologie, Schadstoffe, Bewertungen. Springer, Berlin.
Hunting, E.R., Van der Geest, H.G., 2011. Predictability of bacterial activity and denitrification in aquatic sediments with continuous measurements of redox potential. International Journal of Environmental Science and Technology 8:553-560.
IKSE (Internationale Kommission zum Schutz der Elbe) 2003. Aktionsplan Hochwasserschutz Elbe, Magdeburg.
IUSS/ISRIC/FAO, 2006. World reference base for soil resources, Rome.
Jenne, E.A., 1968. Controls on Mn, Fe, Co, Ni, Cu and Zn concentrations in soils and water, significant role of hydrous Mn and Fe oxides. Advances in Chemistry Series 73:337–387.
Joubert, A., Lucas, L., Garrido, F., Joulian, C., Jauzein, M., 2007. Effect of temperature, gas phase composition, pH and microbial activity on As, Zn, Pb and Cd mobility in selected soils in the Ebro and Meuse Basins in the context of global change. Environmental Pollution 148:749-758.
Junk, W.J., Bayley, P., Sparks, R., 1989. The flood pulse concept in river-floodplain systems. Canadian Special Publications of Fisheries and Aquatic Sciences 106:110-127.
Junk, W.J., Wantzen, K.M., 2004. The Flood Pulse Concept: New Aspects, Approaches, and Applications – an Update, Proceedings of the Second International Symposium on the Management of Large Rivers for Fisheries. RAP Publication. Food and Agriculture Organization and Mekong River Commission, FAO Regional Office for Asia and the Pacific, Bangkok, pp. 117–149.
Kabata-Pendias, A., 2001. Trace elemnts in soils and plants. CRC Press.
Kalbitz, K., Knappe, S., 1997. Influence of soil properties on the release of dissolved organic matter (DOM) from the topsoil. Zeitschrift Fur Pflanzenernahrung Und Bodenkunde 160:475-483.
Kalbitz, K., Wennrich, R., 1998. Mobilization of heavy metals and arsenic in polluted wetland soils and its dependence on dissolved organic matter. Science of the Total Environment 209:27-39.
Keddy, P.A., 2010. Wetland Ecology. University Press, Cambridge.
Klemm, W., Greif, A., Broekaert, J.A.C., Siemens, V., Junge, F.W., Van der Veen, A., Schultze, M., Duffek, A., 2005. A study on arsenic and the heavy metals in the Mulde river system. Acta Hydrochimica Et Hydrobiologica 33:475-491.
Kooistra, L., Leuven, R., Nienhuis, P.H., Wehrens, R., Buydens, L.M.C., 2001. A procedure for incorporating spatial variability in ecological risk assessment of Dutch River floodplains. Environmental Management 28:359-373.
Kools, S.A.E., Berg, M.P., Boivin, M.E.Y., Kuenen, F.J.A., Van der Wurff, A.W.G., Van Gestel, C.A.M., Van Straalen, N.M., 2008. Stress responses investigated; application of zinc and heat to Terrestrial Model Ecosystems from heavy metal polluted grassland. Science of the Total Environment 406:462-468.
Körschens, M., Schulz, E., Klimanek, E.-M., Franko, U., 1990. Die organische Bodensubstanz-Bedeutung, Definition,Bestimmung. Archiv für Acker- und Pflanzenbau und Bodenkunde 41:427-434.
Korte, N.E., Skopp, J., Fuller, W.H., Niebla, E.E., Aleshii, B.A., 1976. Trace element movement in soils: influence of soil physical and chemical properties. Soil Science 122:350-359.
Krueger, A., Neumeister, H., 1999. Schadstoffmobilisierung und Verteilung in Flussauen, Auswirkungen der Veränderungen des geochemischen Milieus nach künstlicher Uberflutung und Grundwasseranstieg. pp. 23–38 In: A. Groengroeft and R. Schwartz (ed.) Eigenschaften und Funktionen von Auenboden an der Elbe. Hamburger Bodenkundliche Arbeiten, 44.
Krueger, F., Groengroeft, A., 2004. The difficult assessment of heavy metal contamination of soils and plants in Elbe river floodplains. Acta Hydrochimica et Hydrobiologica 31:436-443.
Krueger, F., Groengroeft, A., Grunewald, K., Meissner, R., Petzoldt, H., Schwartz, R., 2004a. Pollution of Elbe River floodplains and consequences for future research 11th Magdeburg Seminar on Waters in Central and Eastern Europe. Assessment, Protection, Management, Leipzig.
Krueger, F., Groengroeft, A., Grunewald, K., Meisner, R., Miehlich, G., Petzold, H., Unger, C., 2004b. Auswirkungen der Schadstoffgehalte und Keimbelastung von Hochflutsedimenten auf Böden und Pflanzen. pp. 224–286. In: P. Geller et al. (ed.) Schadstoffbelastung nach dem Elbe Hochwasser 2002, Endbericht des Ad-hoc-Projekts: Schadstoffuntersuchungen nach dem Hochwasser vom August 2002-Ermittlung der Gefahrdungspotentiale an Elbe und Mulde.
*Available at htth://www.ufz.de/hochwasser/bericht/HWEnd.pdf (verified 25 Mar. 2009).*
Krueger, F., Meissner, R., Groengroeft, A., Grunewald, K., 2005. Flood induced heavy metal and arsenic contamination of Elbe river floodplain soils. Acta Hydrochimica et Hydrobiologica 33:455-465.
Krueger, F., Prange, A., Jantzen, E., 1999. Ermittlung geogener Hintergrundwerte an der Mittelelbe und deren Anwendung in der Beurteilung von Unterwassersedimenten. pp. 39–51. In: A. Groengroeft, R. Schwartz (ed.) Eigenschaften und Funktionen von Auenboden an der Elbe. Hamburger Bodenkundliche Arbeiten 44.

Kuntze, H., Herms, U., 1986. Bedeutung geogener und pedogener Faktoren für die weitere Belastung der Böden mit Schwermetallen. Naturwissenschaften 73:195-205.

Kuntze, H., Herms, U., Pluquet, E., 1984. Schwermetalle in Böden - Bewertung und Gegenmaßnahmen. Geologische Jahrbücher. Reihe A 75:715-736.

Lair, G.J., Graf, M., Zehetner, F., Gerzabek, M.H., 2008. Distribution of cadmium among geochemical fractions in floodplain soils of progressing development. Environmental Pollution 156:207-214.

Lair, G.J., Zehetner, F., Fiebig, M., Gerzabek, M.H., Van Gestel, C.A.M., Hein, T., Hohensinner, S., Hsu, P., Jones, K.C., Jordan, G., Koelmans, A.A., Poot, A., Slijkerman, D.M.E., Totsche, K.U., Bondar-Kunze, E., Barth, J.A.C., 2009. How do long-term development and periodical changes of river-floodplain systems affect the fate of contaminants? Results from European rivers. Environmental Pollution 157:3336-3346.

Lamers, L.P.M., Loeb, R., Antheunisse, A.M., Miletto, M., Lucassen, E., Boxman, A.W., Smolders, A.J.P., Roelofs, J.G.M., 2006. Biogeochemical constraints on the ecological rehabilitation of wetland vegetation in river floodplains. Hydrobiologia 565:165-186.

Ledoux, L., Cornell, S., O'Riordan, T., Harvey, R., Banyard, L., 2005. Towards sustainable flood and coastal management: identifying drivers of, and obstacles to, managed realignment. Land Use Policy 22:129-144.

Leser, H., 2003. Geomorphologie. Westermann, Braunschweig.

Lindsay, W.L., 1979. Chemical equilibria in soils. John Wiley and Sons, New York.

Maes, J., Hauck, J., Paracchini, M.L., Ratamäki, O., Termansen, M., Perez-Soba, M., Kopperoinen, L., Rankinen, K., Schägner, J.P., Henrys, P., Cisowska, I., Zandersen, M., Jax, M., La Notte, A., Leikola, N., Pouta, N., Smart, S., Hasler, B., Lankia, T., Andersen, H.E., Lavalle, C., Vermaas, T., Alemu, M.H., Scholefield, P., Batista, F., Pywell, R., Hutchins, M., Blemmer, M., Fonnesbech-Wulff, A., Vanbergen, A.J., Münier, B., Baranzelli, C., Roy, D., Thieu, V., Zulian, G., Kuussaari, M., Thodsen, H., Alanen, E.L., Egoh, B., Sørensen, P.B., Braat, L., Bidoglio, G., 2012. A spatial assessment of ecosystem services in Europe: methods, case studies and policy analysis - phase 2. Synthesis report., Partnership for European Environmental Research Ispra.

Masscheleyn, P.H., Pardue, J.H., Delaune, R.D., Patrick, W.H., 1992. Chromium Redox Chemistry In A Lower Mississippi Valley Bottomland Hardwood Wetland. Environmental Science & Technology 26(6):1217-1226.

Matagi, S.V., Swai, D., Mugabe, R., 1998. A review of heavy metal removal mechanisms in wetlands. African Journal of Tropical Hydrobiology and Fisheries 8:23-35.

McClain, M.E., Boyer, E.W., Dent, C.L., Gergel, S.E., Grimm, N.B., Groffman, P.M., Hart, S.C., Harvey, J.W., Johnston, C.A., Mayorga, E., McDowell, W.H., Pinay, G., 2003. Biogeochemical hot spots and hot moments at the interface of terrestrial and aquatic ecosystems. Ecosystems 6(4):301-312.

Meissner, R., Rupp, H., Schubert, M., 2000. Novel lysimeter techniques - a basis for the improved investigation of water, gas, and solute transport in soils. Journal of Plant Nutrition and Soil Science 163(6):603-608.

Merz, C., Winkler, A., Pekdeger, A., 2009. Trace elements in streambed sediments of floodplains: consequences for water management measures. Environ. Earth Sci. 59(1):25-38.

Meybeck, M., Lestel, L., Bonte, P., Moilleron, R., Colin, J.L., Rousselot, O., Herve, D., de Ponteves, C., Grosbois, C., Thevenot, D.R., 2007. Historical perspective of heavy metals contamination (Cd, Cr, Cu, Hg, Pb, Zn) in the Seine River basin (France) following a DPSIR approach (1950-2005). Science Of The Total Environment 375(1-3):204-231.

Middelkoop, H., 2000. Heavy-metal pollution of the river Rhine and Meuse floodplains in the Netherlands. Geologie En Mijnbouw-Netherlands Journal of Geosciences 79(4):411-427.

Moss, T., Monstadt, J., 2008. Institutional dimensions of floodplains restoration in europe: an introduction. pp. 3-15. In: T. Moss, J. Monstadt (eds.) Restoring floodplains in Europe. IWA Publishing.

Mudroch, A., MacKnight, S.D., 1994. Handbook of techniques for aquatic sediments sampling. CRC Press, Boca Rato.

Mueller, H.W., Schwaighofer, B., Kalman, W., 1994. Heavy-metal contents in river sediments. Water Air and Soil Pollution 72:191-203.

Naiman, R.J., De´camps, H., McClain, M.E., 2005. Riparia: ecology, conservation and management of streamside communities. Academic Press., New York.

Nearing, M.A., Pruski, F.F., O'Neal, M.R., 2004. Expected climate change impacts on soil erosion rates: A review. Journal of Soil and Water Conservation 59:43-50.

Negrel, P., 1997. Multi-element chemistry of Loire estuary sediments: Anthropogenic vs. natural sources. Estuarine Coastal And Shelf Science 44:395-410.

Ng, S., Bloomfield, C., 1962. The effect of flooding and aeration on the mobility of certain trace elements in soils. Plant and Soil 6:108-135.

O'Halloran, K., 2006. Toxicological considerations of contaminants in the terrestrial environment for ecological risk assessment. Human and Ecological Risk Assessment 12:74-83.

Olivie-Lauquet, G., Gruau, G., Dia, A., Riou, C., Jaffrezic, A., Henin, O., 2001. Release of trace elements in wetlands: Role of seasonal variability. Water Research 35:943-952.

Opperman, J.J., Luster, R., McKenney, B.A., Roberts, M., Meadows, A.W., 2010. Ecologically Functional Floodplains: Connectivity, Flow Regime, and Scale. Journal of the American Water Resources Association 46:211-226.

Overesch, M., Rinklebe, J., Broll, G., Neue, H.U., 2007. Metals and arsenic in soils and corresponding vegetation at Central Elbe river floodplains (Germany). Environmental Pollution 145:800-812.

Patrick, J.W.H., Williams, B.G., Moraghan, J.T., 1973. A simple system for controlling redox potential and pH in soil suspensions. Soil Science Society of America Proceedings 37:331-332.

Peijnenburg, W., Jager, T., 2003. Monitoring approaches to assess bioaccessibility and bioavailability of metals: Matrix issues. Ecotoxicology and Environmental Safety 56:63-77.

Petersen, W., Willer, E., Willamowski, C., 1997. Remobilization of trace elements from polluted anoxic sediments after resuspension in oxic water. Water, Air and Soil Pollution 99:515-522.

Pierzynski, G.M., Schwab, A.P., 1993. Bioavailability Of Zinc, Cadmium, And Lead In A Metal-Contaminated Alluvial Soil. Journal Of Environmental Quality 22:247-254.

Poot, A., Gillissen, F., Koelmans, A.A., 2007. Effects of flow regime and flooding on heavy metal availability in sediment and soil of a dynamic river system. Environmental Pollution 148:779-787.

Posthuma, L., Eijsacker, H.J.P., Koelmans, A.A., Vijver, M.G., 2008. Ecological effects of diffuse mixed pollution are site-specific and require higher-tier risk assessment to improve site management decisions: A discussion paper. Science of the Total Environment 406:503-517.

Qu, W.C., Kelderman, P., 2001. Heavy metal contents in the Delft canal sediments and suspended solids of the River Rhine: multivariate analysis for source tracing. Chemosphere 45:919-925.

R Development Core Team, 2011. R: A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria3-900051-07-0 *(URL http:// www.R-project.org/).*

Rate, A.W., Robertson, A.E., Borg, A.T., 2000. Distribution of heavy metals in near-shore sediments of the Swan River estuary, Western Australia. Water Air and Soil Pollution 124:155-168.

Reddy, K.R., Patrick, W.H., 1975. Effect of alternate aerobic and anaerobic conditions on redox potential, organic matter decomposition and nitrogen loss in a flooded soil. Soil Biology and Biochemistry 7:87–94.

Reddy, K.R., Patrick, W.H., 1977. Effect of redox potential and pH on the uptake of cadmium and lead by rice plants. Journal of Environmental Quality 6:259–262.

Rieuwerts, J.S., Thornton, I., Farago, M.E., Ashmore, M.R., 1998. Factors influencing metal bioavailability in soils: preliminary investigations for the development of a critical loads approach for metals. Chemical Speciation and Bioavailability 10:61-75.

Rinklebe, J., 2004. Differenzierung von Auenböden der Mittleren Elbe und Quantifizierung des Einflusses von deren Bodenkennwerten auf die mikrobielle Biomasse und die Bodenenzymaktivitäten von β-Glucosidase, Protease und alkalischer Phosphatase, Martin-Luther-Universität Halle-Wittenberg, Halle, PhD.

Rinklebe, J., Du Laing, G., 2011. Factors controlling the dynamics of trace metals in frequently flooded soils. In: H.M. Selim, 2011.Dynamics and Bioavailability of Heavy Metals in the Root Zone, pp. 245-270, CRC Press. Taylor & Francis Group.

Rinklebe, J., During, A., Overesch, M., Du Laing, G., Wennrich, R., Stark, H.J., Mothes, S., 2010. Dynamics of mercury fluxes and their controlling factors in large Hg-polluted floodplain areas. Environ. Pollut. 158:308-318.

Rinklebe, J., Franke, C., Neue, H.U., 2007. Aggregation of floodplain soils based on classification principles to predict concentrations of nutrients and pollutants. Geoderma 141:210-223.

Rinklebe, J., Heinrich, K., Neue, H.-U., 2001. Der umsetzbare Kohlenstoff als Indikator für die potentuielle bodenmirkobielle Aktivität in Auenböden, Leipzig.

Rinklebe, J., Langer, U., 2006. Microbial diversity in three floodplain soils at the Elbe River (Germany). Soil Biology and Biochemistry 38:2144-2151.

Rohdenbrug, H., 1989. Landschaftsökologie, Geomorphologie. Catena, Cremlingen.

Rommel, J., 2000. Laufentwicklung der deutschen Elbe bis Geesthacht seit ca. 1600. Bundesanstalt für Gewässerkunde, Koblenz.

Rupp, H., Krüger, F., Büttner, O., Kunert, M., Meissner, R., Muhs, K., Witter, B., 2000. Wirkung von Hochwasserereignissen auf die Schadstoffbelastung von Auen und kulturwirtschaftlich genutzten Böden im Überschwemmungsbereich von Oka und Elbe. BMBF-Abschlussbericht. FKZ: 02 WT9617/0 209.

Rupp, H., Rinklebe, J., Bolze, S., Meissner, R., 2010. A scale-dependent approach to study pollution control processes in wetland soils using three different techniques. Ecological Engineering 36:1439-1447.

Salomons, W., 1998. Biogeodynamics of contaminated sediments and soils: Perspectives for future research. Journal of Geochemical Exploration 62:37-40.

Sauve, S., Hendershot, W., Allen, H.E., 2000. Solid-solution partitioning of metals in contaminated soils: Dependence on pH, total metal burden, and organic matter. Environmental Science & Technology 34(7):1125-1131.

Scheffer, F., Schachtschabel, P.E., 2002. Lehrbuch der Bodenkunde. 15th ed. Spectrum, Heidelberg.

Schipper, A.M., Wijnhoven, S., Leuven, R., Ragas, A.M.J., Hendriks, A.J., 2008. Spatial distribution and internal metal concentrations of terrestrial arthropods in a moderately contaminated lowland floodplain along the Rhine River. Environmental Pollution 151:17-26.

Schlichting, E., Blume, H.-P., Stahr, K., 1995. Bodenkundliches Praktikum. Blackwell, Berlin. Blackwell, Berlin.

Scholten, M., Anlauf, A., Buechele, B., Faulhaber, P., Henle, K., Kofalk, S., Leyer, I., Meyerhoff, J., Purps, J., Rast, G., Scholz, M., 2005. The River Elbe in Germany present state, conflicting goals, and perspectives of rehabilitation. Large Rivers 15:579–602.

Scholz, M., Schwartz, R., Weber, M., 2005. Flusslandschaft Elbe - Entwicklung und heutiger Zustand. pp. 5-48. In: M. Scholz, S. Stab, F. Dziock, K. Henle (eds.) Lenebsnräume der Elbe und ihrer Auen. Weißensee Verlag, Berlin.

Schulz-Zunkel, C., Krueger, F., 2009. Trace Metal Dynamics in Floodplain Soils of the River Elbe: A Review. Journal of Environmental Quality 38:1349-1362.

Schulz-Zunkel, C., Krueger, F., Rupp, H., Meissner, R., Gruber, B., Gerisch, M., Bork, H.-R., 2013. Spatial and seasonal distribution of tracemetals in floodplain soils. A case study with the Middle Elbe River, Germany. Geoderma 211–212:128–137.

Schwartz, R., 2001. Die Böden der Elbaue bei Lenzen und ihre möglichen Veränderungen nach Rückdeichung. Hamburger Bodenkundliche Arbeiten. 48, Ph.D.

Schwartz, R., Gerth, J., Neumann-Hensel, H., Bley, S., Forstner, U., 2006. Assessment of highly polluted fluvisol in the Spittelwasser floodplain - Based on national guideline values and MNA-Criteria. Journal of Soils and Sediments 6:145-155.

Schwartz, R., Grongroft, A., Miehlich, G., 2004. Pore water composition as device for the detection of origin and flow direction of soil water in alluvial soils of the Middle Elbe River. Acta Hydrochimica Et Hydrobiologica 31:423-435.

Schwartz, R., Schmidt, B., Miehlich, G., 1998. Einfluß einer Hochwasserwelle auf den Wassergehalt und das Redoxpotential von Auenböden an der Mittelelbe. pp. 257-258. In: W. Geller, P. Punčochář, D. Bornhöft, J. Bouček, H. Feldmann, H. Guhr, V. Mohaupt, M. Simon, J. Smaták, J. Spoustová, O. Uhlmann (eds.) Gewässerschutz im Einzugsgebiete der Elbe. Teubner, Leipzig.

Shaw, T.J., Gieskes, J.M., Jahnke. R.A., 1990. Early diagenesis in differing depositional environments. The response of transition-metals in pore water. Geochimica et Cosmochimica Acta 54:1233–1246.

Shiller, A.M., 1997. Dissolved trace elements in the Mississippi river: Seasonal, interannual, and decadal variability. Geochimica Et Cosmochimica Acta 61(20):4321-4330.

Sims, J.L., Patrick, W.H., 1978. Distribution of micronutrient cations in soil under conditions of varying redox potential and pH. Soil Science Society of America Journal 42:258–262.

Sims, J.T., 1986. Soil-pH eff ects on the distribution and plant availability of manganese, copper, and zinc. Soil Science Society of America Journal 50:367–373.

Smolders, E., Oorts, K., Van Sprang, P., Schoeters, I., Janssen, C.R., McGrath, S.P., McLaughlin, M.J., 2009. Toxicity of trace metals in soils as affected by soil type and aging after contamination: using calibrated bioavailability models to set ecological soil standards. Environmental Toxicology and Chemistry 28:1633-1642.

Soares, H., Boaventura, R.A.R., Machado, A., da Silva, J., 1999. Sediments as monitors of heavy metal contamination in the Ave river basin (Portugal): multivariate analysis of data. Environmental Pollution 105:311-323.

Song, Y.G., Mueller, G., 1995. Biogeochemical cycling of nutrients and trace-metals in anoxic fresh-water sediments of the Neckar River, Germany. Marine and Freshwater Research 46:237–243.

Stanford, J.A., Lorang, M.S., Hauer, F.R., 2005. The shifting habitat mosaic of river ecosystems. . Verhandlungen der Internationalen Vereinigung für Theoretische und Angewandte Limnologie 29: 123–136.

Tack, F.M.G., Van Ranst, E., Lievens, C., Vandenberghe, R.E., 2006. Soil solution Cd, Cu and Zn concentrations as affected by short-time drying or wetting: The role of hydrous oxides of Fe and Mn. Geoderma 137: 83-89.

Tessier, A., Campbell, P.G.C., Bisson, M., 1979. Sequential extraction procedure for the speciation of particulate trace-metals. Analytical Chemistry 51:844–851.

Thonon, I., 2006. Deposition of sediment and associated heavy metals on floodplains. Utrecht Univerisity. Netherlands Geographical Studies 337, Ph.D.

Thornton, J., Abrahams, P., 1983. Soil ingestion. A major pathway of heavy metals into livestock grazing on contaminated land. Science of the Total Environment 28:139–151.

Thorp, J.H., Thoms, M.C., Delong, M.D., 2006. The riverine ecosystem synthesis: Biocomplexity in river networks across space and time. River Research and Applications 22:123-147.

Tiktak, A., Alkemade, J.R.M., Van Grinsven, J.J.M., Makaske, G.B., 1998. Modelling cadmium accumulation at a regional scale in the Netherlands. Nutrient Cycling in Agroecosystems 50:209-222.

Tockner, K., Lorang, M.S., Stanford, J.A., 2010. River Flood Plains Are Model Ecosystems to Test General Hydrogeomorphic and Ecological Concepts. River Research and Applications 26:76-86.

Tockner, K., Malard, F., Ward, J.V., 2000. An extension of the flood pulse concept. Hydrological Processes 14:2861-2883.

Tockner, K., Stanford, J.A., 2002. Riverine flood plains: present state and future trends. Environmental Conservation 29(3):308-330.

Trivedi, P., Axe, L., 2000. Modeling Cd and Zn sorption to hydrous metal oxides. Environmental Science and Technology 34:2215-2223.

Turner, J.N., Brewer, P.A., Macklin, M.G., 2008. Fluvial-controlled metal and As mobilisation, dispersal and storage in the Rio Guadiamar, SW Spain and its implications for long-term contaminant fluxes to the Donana wetlands. Science of the Total Environment 394:144-161.

Van den Berg, G.A., 1998. Geochemical behavior of heavy metals in a sedimentation area of the river Rhine and Meuse. Utrecht University, PhD.

Van den Berg, G.A., Loch, J.P. Gustav, Van der Heijdt, Lambertus M., Zwolsmann, John, J.G., 2000. Geochemical behaviour of trace metals in freshwater sediments. pp. 517-533. In: B. Markert, K. Friese (eds.) Trace elements. Their distribution and effects in the environment. Elsevier, Amsterdam, Lausanne, New York, Oxford, Shannon, Singapore. Tokyo.

Van der Veen, A., Ahlers, C., Zachmann, D.W., Friese, K., 2006. Spatial distribution and bonding forms of heavy metals in sediments along the middle course of the River Elbe (km 287... 390). Acta Hydrochimica et Hydrobiologica 34:214-222.

Van Griethuysen, C., de Lange, H.J., Van den Heuij, M., de Bles, S.C., Gillissen, F., Koelmans, A.A., 2006. Temporal dynamics of AVS and SEM in sediment of shallow freshwater floodplain lakes. Applied Geochemistry 21:632-642.

van Griethuysen, C., Luitwieler, M., Joziasse, J., Koelmans, A.A., 2005. Temporal variation of trace metal geochemistry in floodplain lake sediment subject to dynamic hydrological conditions. Environmental Pollution 137:281-294.

Van Griethuysen, C., Meijboom, E.W., Koelmans, A.A., 2003. Spatial variation of metals and acid volatile sulfide in floodplain lake sediment. Environmental Toxicology and Chemistry 22:457-465.

Van Straalen, N.M., Van Gestel, C.A.M., 2008. A stress ecology framework for comprehensive risk assessment of diffuse pollution. Science of the Total Environment 406:479-483.

Verhoeven, J.T.A., Setter, T.L., 2010. Agricultural use of wetlands: opportunities and limitations. Annals of Botany 105:155-163.

Vidon, P., Allan, C., Burns, D., Duval, T.P., Gurwick, N., Inamdar, S., Lowrance, R., Okay, J., Scott, D., Sebestyen, S., 2010. Hot Spots and Hot Moments in Riparian Zones: Potential for Improved Water Quality Management1. Journal of the American Water Resources Association 46:278-298.

Voegelin, A., Weber, F.A., Kretzschmar, R., 2007. Distribution and speciation of arsenic around roots in a contaminated riparian floodplain soil: Micro-XRF element mapping and EXAFS spectroscopy. Geochimica et Cosmochimica Acta 71:5804-5820.

Vogt, M., Zachmann, D., Treutler, C., Kruger, F., Friese, K., 2000. Zeitliche Belastungsentwicklung von Sedimenten asu Elbaue-Stillgewässern. pp. 209-217. In: K. Friese, B. Witter, G. Miehlich, M. Rode (eds.) Stoffhaushalt von Auenökosystemen. Böden und Hydrologie, Schadstoffe, Bewertungen. Springer, Berlin.

Ward, J.V., Tockner, K., Arscott, D.B., Claret, C., 2002. Riverine landscape diversity. Freshwater Biology 47:517-539.

Ramsar Classification for Wetland Types (2012), *Available at http://www.ramsar.org/cda/en/ramsar-activities-cepa-classification-system/main/ramsar/1-63-69%5E21235_4000_0__(verified 06 Nov 2013)*

Wiens, J.A., 2002. Riverine landscapes: taking landscape ecology into the water. Freshwater Biology 47:501-515.

Xian, X.F., Shokohifard, G.I., 1989. Effect of pH on chemical forms and plant availability of cadmium, zinc, and lead in polluted soils. Water Air and Soil Pollution 45:265–273.

Xiong, L.M., Lu, R.K., 1993. Effect of liming on plant accumulation of cadmium under upland or flooded conditions. Environmental Pollution 79:199–203.

Youssef, R.A., Chino, M., 1991. Movement of metals from soil to plantroots. Water Air and Soil Pollution 57(8):249–258.

Yu, K.W., Bohme, F., Rinklebe, J., Neue, H.U., DeLaune, R.D., 2007. Major biogeochemical processes in soils - A microcosm incubation from reducing to oxidizing conditions. Soil Science Society of America Journal 71:1406-1417.

Yu, K.W., Rinklebe, J., 2011. Advancement in soil microcosm apparatus for biogeochemical research. Ecological Engineering 37:2071-2075.

Zedler, J.B., Kercher, S., 2005. Wetland resources: Status, trends, ecosystem services, and restorability, Annual Review of Environment and Resources. Annual Review of Environment and Resources, pp. 39-74.

Zerling, L., Hanisch, C., Junge, F.W., 2006. Heavy metal inflow into the floodplains at the mouth of the river Weisse Elster (Central Germany). Acta Hydrochimica et Hydrobiologica 34:234-244.

Zuur, A.F., Ieno, E.N., Elphick, C.S., 2010. A protocol for data exploration to avoid common statistical problems. Methods in Ecology and Evolution 1:3-14.

Zuur, A.F., Ieno, E.N., Walker, N.J., Saveliev, A.A., Smith, G.M., 2009. Mixed Effects Models and Extensions in Ecology with R. Springer, New York.

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## Erklärung über die eigenständige Abfassung der Arbeit

Hiermit erkläre ich, dass ich die vorliegende Dissertation, abgesehen von der Beratung durch meine akademischen Lehrer, selbstständig verfasst habe und keine weiteren Quellen und Hilfsmittel als die hier angegebenen verwendet habe. Diese Arbeit hat weder ganz, noch in Teilen, bereits an anderer Stelle einer Prüfungskommission zur Erlangung des Doktorgrades vorgelegen. Ich erkläre, dass die vorliegende Arbeit gemäß der Grundsätze zur Sicherung guter wissenschaftlicher Praxis der Deutschen Forschungsgemeinschaft erstellt wurde.

Kiel, den 23.01.2014

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Christiane Schulz-Zunkel