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STUDYING THE CONTRIBUTION OF URBAN AREAS TO FINE SEDIMENT AND ASSOCIATED ELEMENT CONTENTS IN A RIVER BED

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Studying the contribution of urban areas to fine sediment and associated element contents in a river bed

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Vorwort

An Partikeloberflächen haften Schadstoffe. Partikeltransport ist deshalb Schadstofftransport. Partikelsenken sind Schadstoffsenken, können aber auch zu Schadstoffquellen werden, wenn Erosionsprozesse oder aufgrund von Milieubedingungen Rücklösungsprozesse stattfinden. Je nach Herkunft werden Partikel unterschiedlich beladen. Fließgewässersedimente geben also aufgrund der an den Partikeloberflächen sorbierten Stoffe Auskunft über ihre Herkunft. Der Problemkreis der Ursachen für die Kontamination von Fließgewässersedimenten ist trotz der jahrzehntelangen Forschung zur mechanistischen Beschreibung des Sedimenttransports noch wenig untersucht und verstanden.

Telse David hat im Rahmen der HIGRADE-Graduiertenschule am Helmholtz Zentrum für Umweltforschung (UFZ), Magdeburg, Untersuchungen an Fließgewässersedimenten in der Bode durchgeführt. Die Arbeit wurde von Professor Dietrich Borchardt, der von der TU Dresden und vom UFZ gemeinsam berufener Professor ist, betreut und von Dr. habil. Wolf von Tümpling, UFZ, begleitet.

Telse David hat mit modernen analytischen und statistischen Methoden die Beladung von Sedimenten im Fließgewässer und in Quellen und Eintragspfaden identifiziert. Sie hat durch Fingerprinting, durch eine detaillierte Bestimmung der Partikelbeladung mit Schwermetallen im belasteten Bereich der Flusssedimente, im Mischsystem, im Trennsystem und im Oberlauf des Fließgewässers den Beitrag der Partikelquellen zur Zusammensetzung der Partikelbeladung des Fließgewässers untersucht. Mittels hierarchischer Clusteranalyse, principal component analysis und multivariater statistischer Verfahren ist er ihr gelungen, die Beiträge zu den in den Fließgewässersedimenten gelagerten Stoffen den Quellen zuzuordnen und die damit verbundenen Unsicherheiten abzuschätzen. Auch den Beitrag spezifischer Quellen, wie den Auslass einer Sodafabrik, an den Stoffen im Gewässersediment konnte Frau David quantifizieren.

Den Analysen wurde ein immenses Messprogramm unterlegt: am UFZ in Magdeburg wurden neben bis zu 12 Metallen für alle Proben Kohlenstofffraktionen, CSB, Stickstoff und Phosphor gemessen. Damit wurde eine belastbare Datenbasis geschaffen, die erst durch die aggregierte Darstellung der statistischen Auswertung sinnvoll interpretierbar wurde. Telse David hat auch zur Frage des Vorgehens bei der Interpretation derartiger Datenmengen eine Basis gelegt, auf der zukünftige Arbeiten aufbauen können.

Insgesamt hat Telse David eine wertvolle Doktorarbeit eingereicht, die einen neuen, viel versprechenden Zugang zum Problemkreis des sedimentgebundenen (Schad-)Stofftransports aufzeigt und auch methodisch adäquat absichert.

Preface

Particles are loaded with pollutants and thus, particle transport is pollutants transport. Particle sediments are pollutants sinks, but may however become pollutants sources, when erosion or, due to chemical conditions, re-dissolution processes take place. Depending on their origin, the loading characteristics of particles differ. Therefore, river sediments can be attributed to origins due to pollutants adsorbed at the particles surfaces. The problem on the origin of the river bed sediments contamination is rarely investigated and understood despite the long lasting research on the mechanistic description of sediment transport.

Telse David has carried out investigations on the bed sediments of the river Bode at the Helmholtz Center for Environment Research (UFZ), Magdeburg, in the frame of the graduate school HIGRADE. The work was supervised by Prof. Dietrich Borchardt, who is a Professor jointly appointed by TU Dresden and UFZ, and closely accompanied by Dr. habil. Wolf von Tümpling, UFZ.

Telse David has analysed the loading of sediments in the river bed and in sources and pathways of contaminants with state-of-the-art statistical methods. She has determined the loading pattern – the fingerprint – of sediments with a variety of mostly heavy metals in the sediments of the river downstream and upstream of the immission points as well as in the combined and the separate sewer system in order to estimate the contribution of the sources and the background from upstream to the particle associated contaminants composition. With hierarchical cluster analysis, principal components analysis and multivariate statistics she succeeded to quantify both the contributions of the sources to the pollutants in the river bed sediments and the associated uncertainties. Telse David was also able to show that with her developed method it is possible to quantify the contribution of a specific source such as that of a soda ash industry discharge.

The analysis was based on an extensive measurement program: besides up to 12 metals carbon fractions, COD, nitrogen and phosphorous was measured of all samples. Doing so an extensive data basis was created that became interpretable only by means of the aggregated representation of the statistical analysis. Telse David has also developed a standard for interpretation of this kind of data on which future work can build.

All over, Telse David has submitted a doctoral thesis which opens up a new promising approach to the problem area of sediment bounded pollutants and compounds transport and which also represents an adequate methodological benchmark.

Peter Krebs

Contents

Summary

Urban wet weather discharge impairs the receiving water and sediment quality. Among other factors, particulate matter plays a role. It increases the suspended sediment load of the receiving water and may thus enhance the clogging of the bed sediment which serves as an important river habitat.

This thesis investigates how much urban areas may contribute to the fine sediment and associated element load which is retarded by the bed sediment. It is based on an extensive field study. The study area was the Bode River, a mid-sized stream in Central Germany. About 10 km upstream of the river mouth, the sampling campaign took place close to Staßfurt, a town of 20’000.

During the sampling campaign, the intrusion of fine sediment into the bed sediment was captured by sediment traps. Furthermore three possible sources of this fine sediment were sampled. Within the Town of Staßfurt, we sampled urban wet weather discharge at three sites to capture urban areas. As second source naturally occurring fine sediment was considered. Therefore we took sediment cores upstream of the Town of Staßfurt. As third source, the impact of the upstream catchment was captured by taking suspended sediment samples.

For all sample types, particle-bound element contents were determined to establish element patterns of the receptor and the source sites. The rationale thereby is that the element pattern at the receptor sites results from the element patterns of the sources. Consequently the contribution of the sources can be calculated by mixing models.

In the study area, particulate matter from urban areas is distinct from river borne fine sediment due to elevated copper, zinc, nitrogen and phosphorus contents. We conducted an in-depth analysis of this element pattern by a cluster analysis. It revealed that the particle-bound element pattern is source specific whereby nitrogen, phosphorus and carbon are related to sewage and behave differently than most metals such as copper which mainly originate from surface runoff. The degree to which element patterns agree from site to site is limited by the variability encountered within sample sets from individual sites. Thereby the variability of the element pattern depends on the complexity of the catchment.

The contribution of urban areas to fine sediment and associated elements which were captured by sediment traps was calculated by a mixing model. Based on this mixing model, about 10% of the fine sediment originate from urban areas. Thereby the impact of the Town of Staßfurt could not be detected leading to the conclusion that upstream urban areas contribute most. Because of the elevated content of e.g. copper and zinc, urban areas contribute up to 40% and thus disproportionally high to particle-associated copper and zinc load. The source apportionment of the fine sediment is little influenced by the elements considered in the mixing model. Different element patterns showed that the median contribution of urban areas ranges from 0 – 20%. This lies within the interquartile range of the initial mixing model. Another result of the measurement campaign ist that sediment traps over-estimated the anthropogenic impact because they did not resemble the surrounding bed sediment. When they were exposed, they were completely free from fine sediment and hence served as sink of suspended sediment.

During the sampling campaign, one source was not directly taken into account. It was possible, though, to delineate this source by nonnegative matrix factorization. Within the Town of Staßfurt, a soda ash production site discharges into the Bode River. The nonnegative matrix factorization uncovered that the soda ash production site is a major source of particulate matter and contributes up to 30% of the fine sediment captured by the traps downstream of the Town of Staßfurt. This source dilutes most element contents as it mainly consists of carbonates. This was revealed by studying the element binding according to the BCR extraction scheme.

This thesis shows that urban areas may be a major source of particulate matter and especially associated elements retarded by the bed sediment. It shows that the element contents form a viable pattern to calculate how much urban areas contribute to fine sediment by mixing models. The thesis further shows that nonnegative matrix factorization is a viable tool to delineate such a distinct source as soda ash production site.

Keywords: Urban wet weather discharge; particulate matter; heavy metals; retention; bed sediment; source apportionment

Zusammenfassung

Misch- und Regenwasserentlastungen beeinträchtigen die Qualität von Vorflutgewässern. Unter anderem gelangt Feinsediment während Entlastungsereignissen in Vorflutgewässer. Dieses erhöht die Fracht an suspendiertem Sediment und verstärkt die Kolmatierung der Gewässersohle. Damit ist das hyporheische Interstitial, das ein wichtiges Fließgewässerhabitat ist, vom Eintrag von Feinsediment betroffen.

Diese Arbeit untersucht, wie sehr urbane Flächen zur Feinsedimentfracht und zur Fracht von partikulär gebundenen Elementen beitragen können, die im Bettsediment zurückgehalten werden. Sie beruht auf einer umfangreichen Messkampagne. Das Untersuchungsgebiet dafür war die Bode, ein mittelgroßer Fluss in Mitteldeutschland. Etwa 10 km flussaufwärts der Mündung fand die Messkampagne nahe der Kleinstadt Staßfurt statt.

Im Rahmen dieser Messkampagne haben wir den Eintrag von Feinsediment in das Bettsediment durch Sedimentkörbe erfasst. Drei Quellen dieses Feinsediments haben wir berücksichtigt. In Staßfurt wurden eine Regen- und zwei Mischwassereinleitungen beprobt, um urbane Flächen zu erfassen. Als zweite Quelle wurde natürlich vorkommendes Feinsediment berücksichtigt. Dafür haben wir Sedimentkerne flussaufwärts von Staßfurt genommen. Als dritte Quelle haben wir das stromaufwärts liegende Einzugsgebiet erfasst, indem wir das suspendierte Sediment beprobt haben.

Für alle Proben wurde der Elementgehalt bestimmt, um das Elementmuster des Feinsediments, das ins Bettsediment eingetragen wurde, und der Quellen zu ermitteln. Der Grund für diese Messstrategie war, dass das Elementmuster des Feinsediments in den Körben aus den Elementmustern der Quellen, Regen- bzw. Mischwassereinleitungen, natürlich vorkommendes Feinsediment und suspendiertes Sediment aus dem Einzugsgebiet, resultieren sollte. Damit ist es möglich, den Beitrag über Mischungsmodelle zu berechnen.

Im Untersuchungsgebiet unterscheidet sich das Feinsediment, das von urbanen Flächen stammt, von dem flussbürtigen Feinsediment aufgrund erhöhter Kupfer-, Zink-, Stickstoff- und Phosphorgehalte. Wir haben das Elementmuster der urbanen Flächen mit einer Clusteranalyse genauer untersucht. Dies ergab, dass das partikulär gebundene Elementmuster quellenspezifisch ist, wobei sich

Stickstoff, Phosphor und Kohlenstoff Abwasser zuordnen lassen, während die meisten Metalle wie Kupfer und Zink hauptsächlich aus dem Oberflächenabfluss stammen. Das Maß, zu dem die Muster von Messpunkt zu Messpunkt übereinstimmen, wird durch die Variabilität beschränkt, die die Proben eines Messpunktes aufweisen. Diese Variabilität hängt dabei von der Komplexität des Einzugsgebiets ab.

Über eine Mischungsrechnung konnten wir berechnen, wie viel urbane Flächen zur Fracht von Feinsediment und daran gebundenen Elementen in den Sedimentkörben beitrugen. Im Untersuchungsgebiet stammen etwa 10 % des Feinsediments, das durch die Sedimentkörbe aufgefangen wurde, von urbanen Flächen. Der Beitrag der Stadt Staßfurt konnte dabei aber nicht von dem Beitrag weiter flussaufwärts gelegener urbaner Gebiete getrennt werden. Daraus folgt, dass weiter stromaufwärts liegende Gebiete mehr beitragen als Staßfurt. Wegen des erhöhten Gehalts an z.B. Kupfer und Zink tragen urbane Flächen ca. 40 % und damit überproportional hoch zur partikulär gebundenen Kupfer- und Zinkfracht bei. Für die Berechung des Quellenbeitrags zum Feinsediment spielt es keine große Rolle, welche Elemente in der Mischungsrechnung berücksichtigt werden. Verschiedene Elementmuster ergeben, dass der Medianbeitrag urbaner Flächen zwischen 0 und 20 % liegt. Dies entspricht dem Interquartilsabstand der ursprünglichen Mischungsrechnung. Ein weiteres Resultat der Untersuchungen ist, dass die Sedimentkörbe den anthropogenen Einfluss überschätzten, weil sie das umgebende Bettsediment nicht exakt abbildeten und als Falle funktionierten.

Innerhalb Staßfurts gibt es ein Sodawerk, das seine Produktionsabwässer in die Bode einleitet. Während der Messkampagne wurde diese Quelle nicht direkt erfasst. Es war trotzdem möglich, diese Quelle durch nicht-negative Matrix-Faktorisierung zu identifizieren. Die nicht-negative Matrix-Faktorisierung ergab, dass das Abwasser des Sodawerks eine Hauptquelle des Feinsediments der Bode ist. Bis zu 30 % des Feinsediments in den Sedimentkörben flussabwärts von Staßfurt lassen sich dem Sodawerk zuordnen. Dieses Feinsediment besteht hauptsächlich aus Karbonaten und verdünnt die meisten Elementgehalte. Dies wurde deutlich, indem die Elementbindungen nach dem BCR Extraktionsschema untersucht wurden.

Diese Arbeit zeigt die Relevanz, die urbane Flächen als Quelle von Feinsediment und daran gebundener Elementfracht haben, die ins Interstitial eingetragen werden. Sie zeigt, dass die Elementgehalte ein Muster bilden, mit dem es möglich ist, über eine Mischungsrechnung zu klären, wie viel urbane

Flächen zum Feinsediment beitragen. Die Arbeit zeigt ferner, dass nicht-negative Matrix-Faktorisierung ermöglicht, eine so charakteristische Quelle wie ein Sodawerk zu identifizieren.

Keywords: Misch- und Regenwasserentlastungen; Feinsediment; Schwermetalle; Rückhalt; Bettsediment; Quellenzuordnung

1 Introduction

Urbanization yields high pressure on streams which cause the so called "urban stream syndrome" (Meyer et al. 2005). The urban stream syndrome describes that stream ecosystem functions are deteriorated in urban landscapes. In their review Walsh et al. (2005) summarize that nutrient uptake, organic matter retention and the net ecosystem metabolism is altered. Many stream features are affected by urbanization whereby the interactions and causalities are manifold and complex (Walsh et al. 2005). For instance the channel morphology are altered whereby the complexity is reduced; the hydrological regime also changes whereby the base flow is usually reduced whereas flood frequency and intensity increase; the light regime is altered because riparian vegetation is removed. Additionally the water chemistry changes because nutrients and pollutants are emitted from urban areas. Besides physical and chemical features, a focus of research is the impact of urban areas on biota, especially macroinvertebrates (Klein 1979; Beasley and Kneale 2002; Bilotta and Brazier 2008). In general, the biodiversity decreases whereby the abundance of tolerant species increases at the expense of sensitive species as summarized by Paul and Meyer (2001). For stream ecosystem functioning the hyporheic zone plays a key role. It is an important stream habitat providing shelter and space for biofilm, macroinvertebrates and fish spawn (Orghidan 1959; Stanford and Ward 1988; Hendricks 1993). It is most common to define the hyporheic zone as the sediment adjacent to stream which is influenced by stream water (Findlay 1995; Harvey and Wagner 2000). It thus connects the surface water and groundwater body by hydrological and biogeochemical means and is characterized by biological, chemical and physical gradients (e.g. fauna, concentrations, pH, Temperature, pressure head) (Brunke and Gonser 1997). Fischer et al. (2005) denote the hyporheic zone "river's liver". This indicates that it plays a key role in nutrient retention and matter transformation (Williams et al. 2010; Brunke and Gonser 1997; Boulton et al. 1998). The effective matter transformation within the bed sediment is closely related to hyporheic flow. Hyporheic flow is induced by hydraulic head gradients on different scales (Poole et al. 2006). On a large scale, head gradients between groundwater and surface water induce flow through the interstices (Sophocleous 2002). On a medium scale, stream structures such as riffle and pool sequences generate head gradients (Kasahara and Wondzell 2003; Saenger et al. 2005). On a small scale, streambed heterogeneity which is caused by sand ripples and obstacles induces hyporheic flow (Cardenas et al. 2004; Cardenas and Wilson 2007; Hester and Doyle 2008). As Bencala et al. (2010) point out, the proportion of stream flow involved in hyporheic exchange is in general negligible but the transport of water constituents into the interstices is important. The reason is that the residence time is long and the specific surface area is high within the hyporheic zone compared to the surface water body (Brunke and Gonser 1997). These conditions are favorable for transformation processes.

Urban wet weather discharge plays a key role in deteriorating the hyporheic zone. Particulate matter is emitted during stormwater events which may lead to clogging of the interstices. The deposition and remobilisation of particulate matter are processes naturally occurring in streams. They are site specific influenced by bed morphology, hydraulic conditions, particulate matter concentration and particle size (Schälchli 1993). But these conditions are altered in urban landscapes. Increased particulate matter concentrations may aggravate clogging of the interstices diminishing the permeability of the bed sediment. As the permeability decreases, the water flow and thus the transient storage of organic matter and nutrients is reduced. Consequently the nutrient retention and removal is disturbed (Meyer et al. 2005). Moreover siltation of the bed sediment reduces the refugial space for invertebrates. As a result the population loss increases during floods as imposed by sewer overflows (Borchardt and Statzner 1990).

Particulate matter mainly originates from sewage and is discharged into receiving waters by combined sewer overflow (Welker 2005). Thereby remobilisation of sewer sediment during wet weather flow has to be considered as important source (Dauber and Novak 1982; Crabtree 1989; Gromaire et al. 2001). According to a study by Chebbo et al. (2001) conducted in the Marais catchment in Paris, the mean contribution of sewer sediment to the suspended solid loads in combined wet weather flow reached 63%. Besides sewage and sewer sediment, street runoff also adds to the particle load in sewer overflow. Welker (2005) states that the particulate matter concentrations in street runoff may reach as high concentrations as in sewage. In contrast to sewage, the particulate matter load from street runoff and sewer sediment is supply limited and thus highly dependent on antecedent conditions under which particulate matter deposits.

Particulate matter is not only an important stream quality measure because it changes the suspended sediment load of the receiving water body. Moreover it plays an important role because it carries some pollutants, nutrients and organic matter (Beasley and Kneale 2002). For instance Horowitz (2008) found in urban creeks of the City of Atlanta that more than 75% of the copper, zinc and lead loads are sediment-associated. For this reason, environmental quality norms are defined for sediment-bound contents (Oberflächengewässerverordnung - OGewV 2011). Besides the priority elements arsenic, cadmium, chromium, copper, nickel, lead, mercury and zinc, organic compounds such as biocides, polychlorinated biphenyls or polyaromatic hydrocarbons are also sediment-associated.

Inorganic and organic pollutants result from anthropogenic activities. In 2000 up to 40% of cadmium, copper, lead and zinc load in large German watersheds originated from diffuse urban sources, especially from urban wet weather discharge (Böhm et al. 2001; Fuchs et al. 2002). Sewage treatment plant effluent is not an important source of these metals because they are likely to be particulate matter associated and thus efficiently removed during wastewater treatment (Lester et al. 1979; Stephenson and Lester 1987). Due to the association with particulate matter, the sewer sediment is also an important source of metals. This is even exacerbated because metals adsorb on the sewer sediment during the sewer passage (Chebbo et al. 2001; Gromaire et al. 2001). Metals are widely used in urban areas. The review by Makepiece et al. (1995) describes the concentrations and sources of metals and organic pollutants in stormwater. The habilitation thesis of Welker (2005) also deals with the sources of metals and organic pollutants in urban water systems. In general metal loads in urban wet weather discharge are attributed to three different flow components: sewage, street runoff and roof runoff. Sewage contains considerable amounts of copper, zinc, chromium and nickel (Chebbo et al. 2001; Hillenbrand et al. 2005). These metals are mainly used in plumbing and household appliances. A study by Comber and Gunn (1996) state that plumbing contributes about 93% of the domestic copper load whereas the other metals originate from other household activities. Zinc, for instance, is an important component of personal care products and pharmaceuticals (Sörme and Lagerkvist 2002; Rule et al. 2006). In the Marais catchment, Gasperi et al. (2008) found that the concentrations of most heavy metals (except for Ni) were higher during wet weather discharge than during dry weather flow indicating the relevance of street, yard and roof runoff. Street runoff is mainly polluted by traffic. Brake linings of vehicles contain copper and zinc. Vehicles also release cadmium, chromium, nickel and lead due to tyre wear and combustion (Sansalone and Buchberger 1997; Hjortenkrans et al. 2006; Rule et al. 2006). Crabtree et al. (2006) studied highway runoff and found, however, that only zinc, copper and lead concentrations in street runoff were critical compared to water quality standards in receiving waters. All metals are also used as construction material for e.g. metal roofs and gutters. Consequently runoff from roofs and facades also contribute to the metal load in urban wet weather discharge (Chebbo et al. 2001; Hillenbrand et al. 2005). Catchment characteristics determine how relevant the flow components are in relation to the metal load from urban areas. The type and age of buildings, traffic intensity, street sweeping, type and amount of industrial dischargers are such factors which influence the metal supply. As is the case for particulate matter, antecedent conditions, i.e. longitude of dry weather conditions, also influence the metal supply. Rainfall event characteristics such as rainfall intensity and duration and determine the metal mobilisation (Brezonik and Stadelmann 2002; Soonthornnonda and Christensen 2008).

In contrast to organic pollutants, heavy metals and other inorganic pollutants such as arsenic occur naturally in the environment because of weathering and erosion processes (Reimann and de Caritat 2005). Such geological background contamination may be significant. This is well known for arsenic which exhibits a very high natural spatial variability (Reimann et al. 2009). An important source of inorganic elements is also mining activities (Gäbler and Schneider 2000; Svete et al. 2001). By contrast atmospheric deposition is of little relevance for inorganic elements but has to be considered for organic pollutants such as PAH (Welker 2005).

The toxicity of pollutants depends on their bioavailability. For heavy metals the bioavailability is assessed by sequential extraction schemes. Thereby solvents of different strengths leach the metals according to their mobilisation potential. To allow for comparing findings from different studies, the European Community Bureau of Reference (BCR) introduced a standardized sequential extraction scheme. This scheme consists of three steps and leaches the elements with acetic acid, hydroxylammonium chloride, and hydrogen peroxide and ammonium acetate (Ure et al. 1993; Rauret et al. 1999). Sequential extraction procedures have some limitations which should be considered when interpreting the data. It is acknowledged that the elements may not bind in distinct phases. Moreover it may be difficult to completely and selectively recover the elements from phases (Kheboian and Bauer 1987; Bacon and Davidson 2008). Despite these limitations, sequential extraction schemes are helpful to determine element patterns influenced by anthropogenic impact. In general, elements from urban areas exhibit a higher mobility than elements from natural sources. For example, Virkanen (1998) studied sediment cores in Finland and found that sediment influenced by urbanization binds metals more mobile than pristine sediment. Similarly Hnatuková et al. (2009) detected an increased mobility of copper and zinc downstream of combined sewer overflows in the Czech Republic. Zehetner et al. (2009) investigated the binding of heavy metals across a highway-forest interface and state that traffic-borne metals are more mobile bound than heavy metals from natural sources. The influence of mining activities on the element binding has rarely been studied. Only Svete et al. (2001) investigated the partitioning of elements in a lead and zinc mining area. Their findings indicate that mining, contrary to anthropogenic activities in urban areas, may not influence the mobility of elements.

Particulate matter also carries organic matter and nutrients. The transformation of organic matter may deplete the oxygen concentration in the hyporheic zone. Nutrients such as nitrogen and phosphorus increase the primary production leading to biological clogging of the interstices (Avnimelech and Nevo 1964). As a result the oxygen and matter exchange between the hyporheic zone and the surface water body is reduced so that the habitat quality and thus the ecosystem functioning is deteriorated.

Considering the relevance of the hyporheic zone, the retention of particles in the bed sediment is of importance. Thereby studies in English river stretches have shown that only up to 10% of the annual suspended sediment load is retarded in interstices (Lambert and Walling 1988; Walling et al. 1998; Owens et al. 1999). This agrees with studies about the fate of fine particulate matter. Many of these studies found that the deposition velocity falls short of the sedimentation velocity which indicates that the shear stress inhibits the sedimentation or remobilizes deposited particles (Cushing et al. 1993; Minshall et al. 2000; Thomas et al. 2001). Such remobilization after deposition was directly observed in some field studies (Cushing et al. 1993; Estèbe et al. 1998; Hünken 2006). For instance Cushing et al. (1993) state that 99% of the initially deposited fine particulate organic matter is remobilized within 1.5 to 3 h in two North American streams. As particulate matter from urban areas is enriched in pollutants, this remobilization may cause a secondary pollution (Estèbe et al. 1998). This corresponds to results from a study of the Italian Po River. Davide et al. (2003) observed that the suspended sediment is more polluted during low flow than during high flow conditions. Particulate matter from anthropogenic activities is deposited on the bed sediment surface and thus quickly remobilized and transported. During elevated flow, however, more and deeper interstitial fine sediment, which is less polluted, is remobilized. All these findings suggest that the ingress of particulate matter from urban areas in bed sediment interstices is of little relevance. Moreover urban streams are prone to bank erosion due to altered stream morphology and discharge regime (e.g. Walsh et al. 2005). However, different studies have detected that the bed sediment in urban landscapes is actually polluted with heavy metals (Moon et al. 1994; Birch et al. 2001; Hnatuková et al. 2009). The degree of pollution is often assessed by the enrichment factor. The enrichment factor is the ratio between measured element content and background contamination and was first introduced by Zoller et al.

(1974) to assess air pollution at the South Pole. The enrichment factor, however, only allows to address the anthropogenic impact by qualitative means.

The circumstance that fine sediment carries elements allows to quantify the source contributions to fine sediment and sediment-bound pollution. Thereby two different approaches exist. Both assume that the element pattern of the sediment results from the mixing of source patterns. It is therefore necessary that the sources exhibit distinct element patterns. In water research, the first approach is usually called sediment tracing, composite fingerprinting or multivariate mixing modeling (Walling et al. 1993; Collins et al. 1997; Motha et al. 2003). In air pollution studies the term chemical mass balance is common (Henry et al. 1984), in geological studies end-member modelling (Weltje 1997). Thereby the sources are known and their element patterns are determined. Their contribution is then calculated by linear mixing. A critical point is that source patterns may alter before reaching the receptor site because of biogeochemical processes. This was already addressed by Friedlander (1973). Some studies take this into account by correcting the contents for particle size, organic matter content and even element specific fate (Collins et al. 1997; Motha et al. 2002). Multivariate mixing modeling is mainly applied for suspended sediment transport studies whereas the bed sediment has not been considered as receptor so far. Most studies were thereby undertaken in rural areas so that urban areas as sources were neglected. Only Carter et al. (2003) conducted a study in an urbanized catchment and considered road dust and sewage treatment plant effluent as sources. Sediment tracing has also barely been applied to apportion the sources of sediment pollution. Only Walling et al. (2008) used multivariate mixing modeling to study sources of particulate phosphorus in English river catchments.

In studies about sediment pollution, another approach is mainly followed. This approach is called multivariate receptor modeling (Henry et al. 1984; Henry 2002). It is applied when the sources are difficult to monitor or even unknown. In this case multivariate statistics decompose the receptor pattern into source characterization and contribution patterns (Hopke et al. 1976; Hopke 2003; Tauler et al. 2009). Principal component analysis, factor analysis, positive matrix factorization and multicurve resolution are used to decompose the receptor pattern. Multivariate receptor modeling has been widely used in air pollution studies (see review by Chow and Watson 2002). It is less common in water research. But this approach has been applied in some studies to identify sources of organic and metal pollution in river sediment (Evans et al. 1990; Peré-Trepat et al. 2006; Leopold et al. 2008). A critical issue of multivariate receptor modelling is to decide on the number of sources. Moreover the identification and interpretation of the sources may be difficult.

The impact of urban areas is long acknowledged and mitigation measures are implemented. Thereby the Water Frame Directive (CEC 2000) evoked a change in urban water management. Instead of regulating the load of emission according to the state of the art, integrated urban water management additionally considers the impact of emissions. In Germany, the technical rules of the BWK are the most sophisticated. They consider hydraulic stress, oxygen demand, ammonia toxicity, phosphorus concentration and pathogenic germs as criteria to evaluate the impact of urban areas. Particulate matter emissions are also acknowledged as stressor but no target values are defined (BWK 2007; BWK 2008). In Switzerland, by contrast, frequency-duration-based target values for particulate matter are defined according to the response of the receiving water for combined sewer overflows (VSA 2007). Thereby the toxicity of particulate matter due to particle associated pollutants (particulate matter exceeding 25 g/m^2 bed sediment for less than 5% of the year), the deteriorating effects of clogging (particulate matter exceeding 625 g/m^2 bed sediment for less than 20% of the year) and the induced oxygen demand (organic matter exceeding 2.4 g/m^2 bed sediment for less than 10% of the year) are considered.

To implement such target values in Germany as well, they need to be validated based on the impact of urban areas on the stream quality. It is therefore necessary to determine how much urban areas contribute to the fine sediment load of receiving water bodies. It is furthermore essential to quantify how much particulate matter from anthropogenic activities is transported into the hyporheic zone as a very important stream habitat. In my thesis, I investigate the contribution of urban areas to fine sediment in a receiving water body based on a field study. During the field study, urban wet weather discharge and the ingress of fine sediment in the bed sediment were monitored. A focus lied on particulate matter bound element patterns to apportion the sources of fine sediment and sediment-associated pollution.

The study area was the Bode River at the Town of Staßfurt. Staßfurt has a population of 20 000 and is situated about 10 km upstream of the river mouth into the Saale River. The Bode River is a highland river draining the Northern Harz Mountain Range and flowing through arable land. Around the Town of Staßfurt, it exhibits a moderate to poor ecological status according to European environmental standards (MLU 2005). Former mining activities in the Harz Mountains characterize the water chemistry of the Bode River network as measurements by the Helmholtz Centre for Environmental Research (UFZ) reveal. Thereby reservoirs in the Harz Mountains retain a considerable load of heavy metals and organic matter. Additionally the tributary Selke exhibits elevated arsenic and lead concentrations. Besides the mining influence, the Bode catchment is a typical situation for Germany. About 10% of the catchment is impervious. These areas are drained by both combined and separate sewer systems. Besides Staßfurt, additional towns of medium sizes are situated in the Bode River catchment. The towns of Oschersleben, Quedlinburg and Halberstadt have populations between 20 000 and 40 000. In addition to domestic and stormwater effluent, a soda ash production site discharges its cooling and production waste water into the Bode River in Staßfurt. The Town of Staßfurt was chosen for the research activities because the urban wet weather discharges are expected to deteriorate the stream water quality according to the BWK water quality modelling tool VERENA. Moreover, the Bode River catchment is the study area of the Helmholtz terrestrial observatory TERENO.

In chapter 2, I characterize the particulate matter emissions from urban wet weather discharge by means of its particle-associated element pattern. This provides an aid to determining its impact on receiving surface waters. During a six months measurement campaign, we determined particle-associated concentrations of major pollutants and rare earths for three combined water/stormwater outlets in the town of Staßfurt. We differentiated the particle-associated constituents on the basis of a hierarchical cluster analysis. Repeating the cluster analysis on random subsets, we gained information about the variability of the element patterns between and within the sites.

Chapter 3 deals with the contribution of urban areas to fine sediment captured by sediment traps up- and downstream of the Town of Staßfurt. To quantify how much fine sediment originates from urban areas, we used a multivariate mixing model. In a first step, it is determined whether the sources "urban areas", "local background" and "upstream catchment" are distinct and should be considered in the mixing model. Then the source contributions to fine sediment and associated elements are calculated. The results are used to assess the relevance of urban areas concerning the fine sediment load and the pollution with priority elements. Furthermore, the impact of biogeochemical processes on the calculation is assessed.

Chapter 4 focuses on the impact of the soda ash production effluent on the fine sediment load of the Bode River. It highlights whether such an industrial point source has to be considered in sediment management. In this context the bioavailability of priority elements is also taken into account to discuss the impact of the soda ash industry effluent. To identify the contribution of the soda ash production effluent, we used a multivariate receptor model because only limited prior knowledge about the sources is necessary. The bioavailability of priority elements is assessed by the remobilisation potential according to the BCR extraction scheme.

In chapter 5 the findings of the field study are briefly summarized, conclusions are drawn and an outlook is given.

2 Element patterns for particulate matter in stormwater effluent

2.1 Introduction

Stormwater impairs stream water and sediment quality. This is a matter of concern in that stormwater is a major source of pollutants such as heavy metals. For instance, a study conducted by (Fuchs et al. 2002) revealed that in 2000 33% of the Hg and Cd load in major German watersheds originated from diffuse urban sources predominantly on account of stormwater.

Some metals such as Cu, Pb and Zn associate readily with particulate matter (e.g. Horowitz et al. 2008; Gasperi et al. 2009). Consequently, recent studies have been focussed on particulate emissions and associated pollutants in stormwater (e.g. Chebbo et al. 2001; Gasperi et al. 2008; Kafi et al. 2008). It has been shown that the stormwater pollutants mainly originate from runoff and sewer sediment. The crucial role played by processes in the sewer was highlighted as well. In such cases the runoff mixes with sewage and interacts with the sewer sediment. The fraction of particle-bound metals increases through adsorption and precipitation (Chebbo et al. 2001; Houhou et al. 2009). Furthermore, studies show that sewer sediments act as both source of as well as sinks for particulate matter, nutrients and pollutants (Chebbo et al. 2001; Gromaire et al. 2001; Houhou et al. 2009).

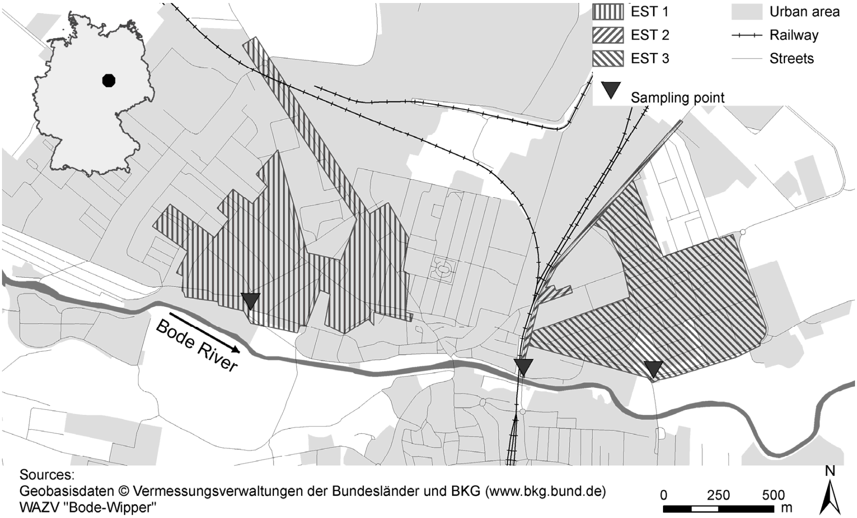
To assess the impact of stormwater particulate matter on river water and sediment quality, it is important to trace the fate of particulate matter in receiving waters. The application of source apportionment models represents a promising approach as such models have been developed into well-tried tools in sediment budget research (Walling 2005). To this end it is necessary to characterize the stormwater by means of the particle-associated element patterns rather than by single constituents. In contrast to total concentrations and their dynamics, however, little is known about the behaviour of particulate concentrations.

In this chapter, we report on the characterization of stormwater based on the element patterns for particulate matter in three effluent discharges from a German town. We mainly focus on inorganic constituents such as heavy metals and rare earths. In addition, we consider nitrogen, carbon and phosphorus.

2.2 Materials and methods

2.2.1 Sampling campaign

The sampling sites were located in Staßfurt, a town of approx. 20,000 in central eastern Germany. Staßfurt is situated in the rain shadow of the Harz mountain range and has an annual precipitation of 470 mm. Its sewer system consists of approx. 50% each of combined and separate sewers. In the northern part, three stormwater outlets which discharge into the Bode River were equipped with automatic samplers and flow meters (6700 Sampler and 750 Area Velocity Module of Teledyne Isco, US) as shown in Figure 4.1.



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WAZV "Bode-Wipper"

Figure 2.1: Study site Staßfurt showing the three catchments and sampling points.

The investigated catchments differ mainly in their areas and the sewer-type proportions (Table 2.1). The outflow from the smallest catchment EST2 is dominated by a separate sewer which for the most part drains a street. It also receives the outflow from a septic tank.

Table 2.1: Catchment characteristics of the three sampled stormwater outlets.

		EST1	**EST2**	**EST3**
Population equivalent	(-)	1800	34	1200
Catchment area	(ha)	60.0	3.6	46.5
Impervious area	(ha)	18.6	3.4	15.5
Length of combined sewers	(m)	6000	280	3210
Length of separate sewers	(m)	160	1790	3580
Industrial discharger	(-)	-	-	Food industry
Sampled events:				
< 5 mm precipitation	(-)	10	4	4
5 - 10 mm precipitation	(-)	8	4	4
10 - 20 mm precipitation	(-)	4	0	1

Samples were taken volume-proportional depending on the site after 10 to 100 m³ flow. A sample comprises two sub-samples of 400 ml. From July 2009 until December 2009, between 8 and 22 events per site were sampled. The precipitation of these events ranged from 0.6 to 20.0 mm.

2.2.2 Analytical procedure

The samples were analyzed for dry weight suspended solids (SS) in accordance with German Industrial standards (DIN38409-2). Rare earths (Pr, Nd, Lu, La, Ho, Hf, Gd, Eu, Er, Dy, Ce, Sm, Yb, Tm, Tb), the actinoid Th and metals (Zn, Pb, Fe, Cu, Cd, Al, Ti) were determined after microwave digestion with HNO_3/H_2O_2 as total concentration and filtration (<0.45 µm) as dissolved fraction using mass spectrometry with inductive coupled plasma (Agilent 7500c, Agilent Technologies, US). COD was determined using cuvette tests (Hach Lange, Germany), organic and inorganic carbon was determined as total concentration (TOC and TIC) and after filtration as dissolved fraction using a carbon analyzer (Dimatoc2000, Dimatech, Germany). Total nitrogen (TNb), ammonia, nitrate and nitrite and soluble phosphorus were determined using continuous flow analysis (Skalar, The Netherlands). Total phosphorus (TP) was determined using a photometer (CADAS200, Hach Lange, Germany). The particle-associated concentrations were calculated as the difference between total and dissolved concentrations divided by SS concentrations.

2.2.3 Data analysis

Data analysis was carried out in the statistical environment R (v. 2.10.1) using the packages stats and clue (Hornik 2009; R Development Core Team 2009). To determine the significance between the three sampling sites concerning total and particle-associated concentrations of single constituents, we performed permutation tests.

We used hierarchical cluster analysis according to Ward's method to establish the particle-associated element patterns. To this end the data set was reduced so that each stormflow event provides only one data point per sampling site. The value used in each case was the median event concentration. Except for nitrogen, La and Nd, the data were log-transformed so that the parameters were normally distributed. Before calculating the squared Euclidean distance between the constituents as a measure of dissimilarity, the data were standardized. Most rare earths, Th and Cd were excluded from the cluster analysis. In many cases these constituents could not be quantified.

For each outlet a dendrogram was calculated on a subset of 90% of the site-specific data set. The subset was chosen randomly. This procedure was repeated 1000 times so that a dendrogram ensemble was produced for each outlet. This dendrogram ensemble was merged into a site-specific dendrogram by minimizing the Euclidean dissimilarity between the associated ultrametrics. Similarly, a dendrogram across all three sites was computed by merging all three site-specific dendrogram ensembles. The resulting site-specific dendrograms were compared with each other by computing the γ coefficient as a measure of association (Hornik 2009). The γ coefficient is calculated as $1 - d$ where d is the rate of discordant ranks of a pair of constituents between two dendrograms. We also calculated γ within each dendrogram ensemble to assess the within-site variability of the element pattern. This procedure was also followed for subsets containing 30% and 50% of the available data, respectively.

2.3 Results and discussion

2.3.1 Total concentrations

The stormwater effluent quality is comparable to stormwater effluent quality reported elsewhere (e.g. Makepeace et al. 1995; Chebbo et al. 2001; Gromaire et al. 2001; Kafi et al. 2008). The main differences between the three effluents are caused by parameters which are closely related to sewage such as COD, TIC, TOC, TNb and TP. In general, the median concentrations and the dispersions are significantly lowest at EST2 ($p<0.05$). This can be explained by the circumstance that only primary treated sewage from a septic tank is discharged into this sewer system.

Outlet EST3 can be distinguished from the other two outlets EST1 and EST2 in that it exhibits higher median SS and metal concentrations (Table 2.2). The results are significant for SS, Al, Cu, Zn and Ti ($p<0.05$). Considering that EST3 has a higher percentage of separate sewers, more discharge originates from runoff compared to EST1. This may explain the higher metal concentrations. EST3 and EST1, however, exhibit similar concentrations for sewage constituents. This suggests that less extraneous water infiltrates the sewer system of EST3.

Table 2.2: The 10th, 50th and 90th percentile of the total concentrations of constituents in the three stormwater effluents.

		EST1 n = 55			EST2 n = 23			EST3 n = 38		
		P_{10}	P_{50}	P_{90}	P_{10}	P_{50}	P_{90}	P_{10}	P_{50}	P_{90}
SS	mg/l	66	174	965	58	140	476	153	356	568
COD	mg/l	60	219	767	39	81	174	116	290	548
TIC	mg/l	16.4	25.0	48.8	12.4	15.5	18.5	19.3	33.0	50.6
TOC	mg/l	7.2	34.2	300	5.2	14.5	38.3	18.2	80.5	157
TNb	mg/l	3.1	10.5	28.4	3.0	4.9	8.8	5.6	11.7	26.8
TP	mg/l	<0.06*	1.31	5.83	<0.06*	<0.06*	1.11	0.70	2.66	5.19
Al	µg/l	1420	3915	18500	1754	3790	10028	4490	9894	13540
Fe	µg/l	1274	3255	10940	1897	4060	12506	3570	6125	12400
Cu	µg/l	28.6	81.0	529	33.2	54.5	149	63.4	155	274
Zn	µg/l	126	337	1384	171	336	1137	280	537	704
Cd	µg/l	<0.2*	<0.2*	0.4	<0.2*	<0.2*	<0.2*	<0.2*	<0.2*	<0.2*
Pb	µg/l	6.4	18.5	62.4	7.1	9.3	39.3	9.8	16.6	35.5
Ti	µg/l	10.7	50.8	261	45.8	97.0	251	28.3	165	270
Ce	µg/l	0.9	3.3	11.1	2.7	4.2	10.6	1.1	6.5	13.9
La	µg/l	0.5	1.7	6.0	1.4	2.3	5.6	0.6	3.5	7.5
Nd	µg/l	<0.5*	1.4	4.9	1.1	1.9	4.7	0.5	2.9	6.1

* denotes limit of quantification

Cd values generally remained below the limit of quantification and could be quantified for only a few events at EST1 (Table 2.2). Most rare earths and Th were also mainly detected below the limit of quantification and are thus not shown in the table.

2.3.2 Particle-associated concentrations

Little literature exists on the particle-associated concentrations for pollutants. Studies in Paris report mean Zn, Cd and Pb concentrations of combined sewer overflow which are at least 80% higher than the median concentrations of the effluents sampled during our study (Estèbe et al. 1998; Kafi et al. 2008). Only the median Cu concentration is comparable. Jartun et al. (2008) analyzed surface runoff in Bergen, Norway. Except for Pb the mean concentrations reported by these researchers are well below the median concentrations which we determined (Table 2.3).

Table 2.3: The 10th, 50th and 90th percentile of the particle-associated concentrations of constituents in the three stormwater effluents.

	EST1 n = 55			**EST2** n = 23			**EST3** n = 38		
	P_{10}	P_{50}	P_{90}	P_{10}	P_{50}	P_{90}	P_{10}	P_{50}	P_{90}
COD mg/g SS	399	799	1265	157	315	852	380	574	1087
IC mg/g SS	5	27	80	LOQ	3	38	12	22	36
OC mg/g SS	8	75	257	8	31	120	50	148	238
N mg/g SS	23	40	65	10	25	57	21	40	54
P mg/g SS	<1*	6	8	<1*	<1*	3	1	6	8
Al µg/g SS	12158	19717	37909	16018	29210	41488	20132	28958	36894
Fe µg/g SS	7184	18982	32884	19885	29835	50537	13513	21069	27983
Cu µg/g SS	259	539	725	170	370	608	257	461	752
Zn µg/g SS	826	1467	2709	992	2116	4695	1178	1419	2070
Cd µg/g SS	<1*	<1*	1	<1*	<1*	<4*	<1*	<1*	<1*
Pb µg/g SS	45	100	144	58	115	160	31	64	84
Ti µg/g SS	184	428	860	478	760	1120	447	620	891
Ce µg/g SS	5	15	29	17	29	49	14	20	44
La µg/g SS	<4*	7	15	9	15	23	5	11	23
Nd µg/g SS	<2*	5	12	5	12	18	4	8	17

* denotes limit of quantification

EST2 can be distinguished from the other two outlets in respect of the parameters associated with sewage. The EST2 particles are significantly least loaded ($p<0.05$) with COD, inorganic and organic carbon (OC and IC), nitrogen (N) and phosphorus (P) because the outlet mainly receives runoff. This pattern was also revealed when considering the total concentrations.

Regarding the metals, the pattern of the particle-associated concentrations differs from the pattern of the total concentrations. EST3 exhibited the highest total metal concentrations. But the particle-associated concentrations are similar to those of EST1. In fact EST2 differs from EST1 and EST3 in that its particles are more heavily loaded with most metals. The results are significant for Fe, Zn, Ce, La and Nd ($p<0.05$). This indicates that the runoff introduces highly polluted particles at EST2. EST3 differs from the other two outlets as the particle-associated Fe, Pb and Zn concentrations exhibit a significantly lower variability compared to the outlets EST1 and EST2.

2.4 Particle-associated element patterns

2.4.1 Element pattern across the three outlets

We focus on the particle-bound concentrations as we are particularly interested in the bed sediment quality of the receiving water body. The element pattern based on the particle-associated concentrations is characterized by two different source-specific groups (Figure 2.2a). The first group comprises organic carbon (OC), nitrogen (N), COD, inorganic carbon (IC), phosphorus (P) and Cu. These compounds are associated with sewage and sewer sediment (Chebbo et al. 2001; Gromaire et al. 2001). Based on the cluster analysis, however, the sewer sediment and sewage cannot be distinguished from each other. The second group consists of the remaining metals and is associated with runoff (Chebbo et al. 2001).

Some aspects of the particle-associated element patterns are spatially very consistent. Cu and OC proved to be strongly associated with each other, a result which agrees with those obtained for three rivers in the USA (Shi et al. 1998). The metals Al, Fe, Ti and Ce are always partitioned into a group, and La and Nd are closely related (Figure 2.2b-d).

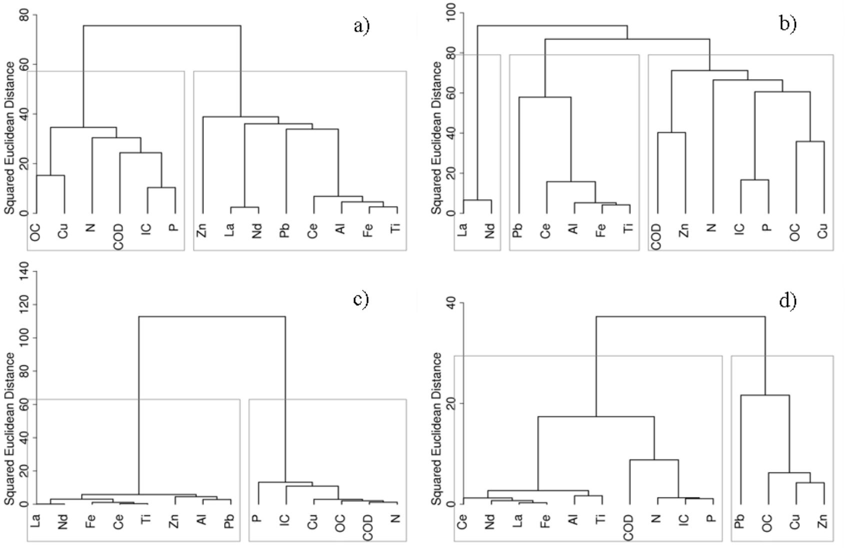


Figure 2.2: Particle-associated element patterns based on 1000 hierarchical cluster analyses on randomly chosen 90% subsets across the outlets EST1, EST2 and EST3 (a), at the outlet EST1 (b), EST2 (c) and EST3 (d).

On the other hand, the partitioning results for some constituents differ from site to site. At EST1 Zn is partitioned along with constituents related to sewage such as COD. At EST3 Pb and Zn are related to OC and Cu, whereas the other sewage constituents belong to the group of most metals. These two catchments are larger, have a higher percentage of combined sewers and are consequently more complex than catchment EST2. In these catchments, it is possible that flows arising from different sub-catchments hinder a more definite classification of the constituents. Moreover, at EST3 the elements cannot readily be separated from each other, as indicated by the low squared Euclidean distance.

2.4.2 Between-site and within-site variability

The particle-associated element patterns between the sites differ from each other in a manner which is at variance with the particle-associated concentrations of single constituents. With regard to the element patterns, outlet EST2 agrees better with both EST1 and EST3 than EST1 and EST3 with each other (Figure 2.3a).

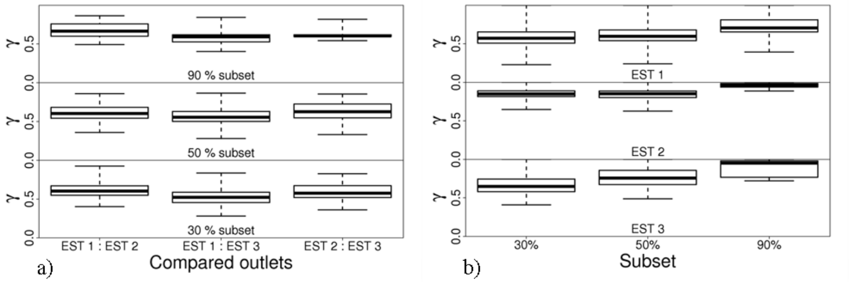


Figure 2.3: Agreement between the outlets EST1, EST2 and EST3 based on the γ coefficient of 1000 dendrograms (a) and agreement within the 1000 dendrograms at each outlet (b) (The median is shown as a broad bar, the boxes cover the interquartile range, and the whiskers extend to minimum and maximum values).

There are major differences in the particle-associated element patterns for EST2 and EST3. Their element patterns agree equally well with a median γ of 0.6 irrespective of the percentage of data used for the cluster analysis (Figure 2.3a). However, the agreement within the sites increases with the percentage of data used. The 90% subsets yield a high intra-site median agreement of 0.95 (Figure 2.3b). In contrast, the relatively high within-site variability of the element pattern at EST1 places limits on the degree of association between EST1 and the other two outlets.

The within-site variability of the element pattern depends on the catchment complexity. The outlet EST2, which is small and of little complexity, separates the source-specific groups very efficiently. Consequently, EST2 exhibits the highest median γ irrespective of the subsets considered. In contrast, the element pattern of EST1 varies most and thus yields the lowest degree of agreement. Even the dendrograms on randomly chosen 90% subsets reach only a median γ of 0.75 (Figure 2.3b). The reason for such variable behaviour in the constituents is probably to be found in the mixing of runoff, sewage and mobilised sewer sediment from different sub-catchments.

2.5 Conclusions

The study shows that there are grounds for regarding the particle-bound concentrations and their patterns as representing suitable stormwater quality measures to aid tracking of the impact of stormwater particles on receiving waters. In our study constituents associated with sewage and sewer sediment exhibit behaviour which differs from that of constituents associated with runoff. This pattern, however, is not consistent. For instance the partitioning of Zn and Pb differs between the sampled sites.

Consideration of the particle-associated element patterns leads to a different assessment of the stormwater quality as compared to the consideration of water-phase concentrations. The separate sewer-dominated outlet can be clearly separated from the other two outlets on the basis of the particle-associated concentrations of single constituents. However, based on the particle-associated element pattern it agrees better with the combined sewer overflows than the combined outlets agree with each other.

There are major differences in the element patterns between two sites. High within-site variability, however, limits the degree of agreement between sites. The within-site variability depends on the catchment characteristics and complexity.

3 Urban wet weather discharge as source of sediment-associated elements in a river bed

3.1 Introduction

The bed sediment is an important river habitat and plays a key role in the transformation of nutrients and organic matter (Brunke and Gonser 1997). Urban wet weather discharge from urban areas may deteriorate this habitat by emitting particulate matter and associated pollutants. Studies found that the contents of heavy metals such as Zn, Cu and Pb are elevated in river bed sediments as a consequence of stormwater and combined sewer overflows (Moon et al. 1994, Birch et al. 2001; Davide et al. 2003; Kronvang et al. 2003; Hnatuková et al. 2009). The enrichment of trace metals compared to background concentrations has been widely applied to assess the anthropogenic impact on sediment quality (e.g. Sharma and Subramanian 2010, Peng et al. 2011). Recent studies further used multivariate statistics to identify anthropogenic sources of sediment pollution (Zhou et al. 2007, Alaoui et al. 2010). But it is usually difficult to interpret and identify the sources derived from multivariate statistics. Because of this, another approach is of interest to quantify how much anthropogenic and especially urban areas contribute to sediment pollution. Multivariate mixing modelling of composite fingerprints has been successfully used in quantitative studies dealing with the source apportionment of sediment. This approach has been barely used to quantify source contributions to sediment pollution. Only Walling et al. (2008) conducted a study to apportion the sources of particulate phosphorus in UK river catchments.

Mixing models are appealing due to their straight forward concept and simplicity. This, of course, is to the extent of neglecting biogeochemical processes which was already addressed in an early air pollution study by Friedlander (1973). Elements partition rapidly between dissolved and particulate phase so that the fate of pollutants associated with fines deviate from the fate of fines (Gagnon and Saulnier 2003). This is influenced by the change in particle size and content of organic matter during the generation of fines and their transport. For this reason Collins et al. (1997) introduced factors to take the particle size and organic matter selectivity into account. Motha et al. (2002) further introduced parameter specific factors to take their individual fate into account.

Most studies about sediment tracing focus on suspended sediment rather than bed sediment. This is due to the fact that, from a sediment balance perspective, the bed sediment is of minor importance. Studies in UK river stretches found that only up to 10% of the total annual suspended sediment load are retarded in interstices of the bed sediment (Lambert and Walling 1988; Walling et al. 1998; Owens et al. 1999). However, such sediment balances do not consider the adverse effects of retarded toxicants, the clogging of interstices or oxygen depletions in the hyporheic zones and thus the loss of bed sediment as habitat for biota.

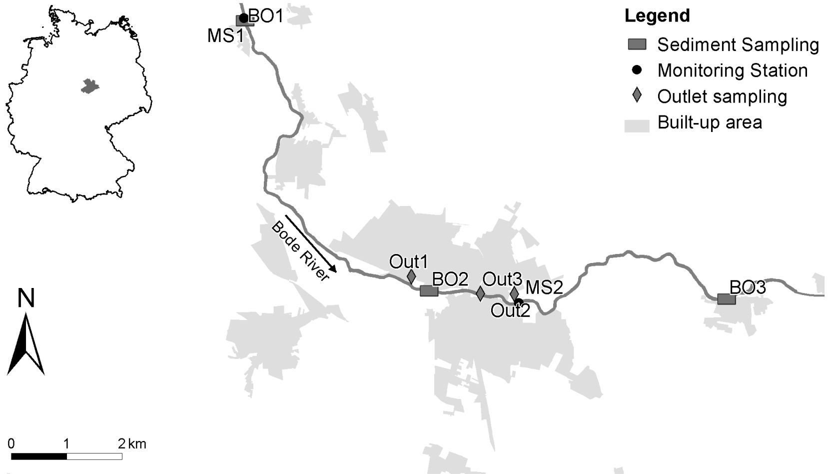
This chapter reports how much urban wet weather discharge contributes to the accumulation of fines and associated element pollutants in the receiving bed sediment of a river stretch of Middle Germany. The main objectives of the study are to (1) describe the composite fingerprints of the sources of fine sediment by nutrient and element contents based on a principal component analysis; (2) quantify the contribution of urban areas to fine sediment and associated pollutants captured by bed sediment traps using a mixing model of composite fingerprints; (3) assess the relevance of urban areas for priority pollutants for which national sediment quality standards are defined; (4) assess the uncertainty of the mixing model results related to the setup of the mixing model and biogeochemical processes.

3.2 Materials and methods

3.2.1 Sampling campaign

The study area is the lower reach of the Bode River close to the Town of Staßfurt (Figure 3.1). The Bode River drains the Northern Harz mountain range and merges into the Saale River. It is a mid-sized fine to coarse substrate dominated siliceous highland river. In Staßfurt, it has a catchment of 3200 km^2 and an average discharge of 13.0 m^3/s. Arable land covers in total 62% of the catchment. 21% of the catchment, especially in the Harz Mountains, are forest.

The lower reach of the stream has a sandy to gritty sediment and exhibits a moderate to poor ecological status according to European environmental standards (Minestry of Agriculture and the Environment of the State Saxony-Anhalt 2005). Due to former mining activities in the Harz, the Bode river and especially its tributary the Selke River is characterized by elevated metal concentrations such as Cu, Zn, As and Pb. Within Staßfurt a soda ash production site discharges into the Bode River.



Sources:
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Wasser- und Abwasserzweckverband "Bode-Wipper"

Figure 3.1: Location of Bode catchment and sampling sites.

At the sites (BO1, BO2 and BO3) bed sediment traps were installed to capture the intrusion of fine sediment as described by Lisle (1989) and Sear (1993). The rationale to use these traps was to get a sample of fine sediment intruded over a clearly defined time span. A sediment trap consisted of a wire basket of a mesh size of 2-3 mm filled with sieved bed sediment. They were exposed for 3-10 months (Figure 3.2). At the sampling sites BO 1 and BO2 five sediment traps were installed across the river width, at BO3 four. To allow for a relatively easy lifting and exchange of the baskets, they were put into a second larger outer basket and a bag of nylon was stored underneath the trap. When lifting the sediment traps, a water grab sample was taken at each site to study the suspended sediment. At BO1, three sediment cores were taken. At two monitoring stations (MS1 and MS2) time proportional water samples were taken to study the suspended sediment during elevated discharge. Within the town of Staßfurt, three urban wet weather outlets (Out1, Out2 and Out3) were sampled with automatic samplers from June 2009 to March 2010. Further details about the sampling strategy are described in David et al. (2011).

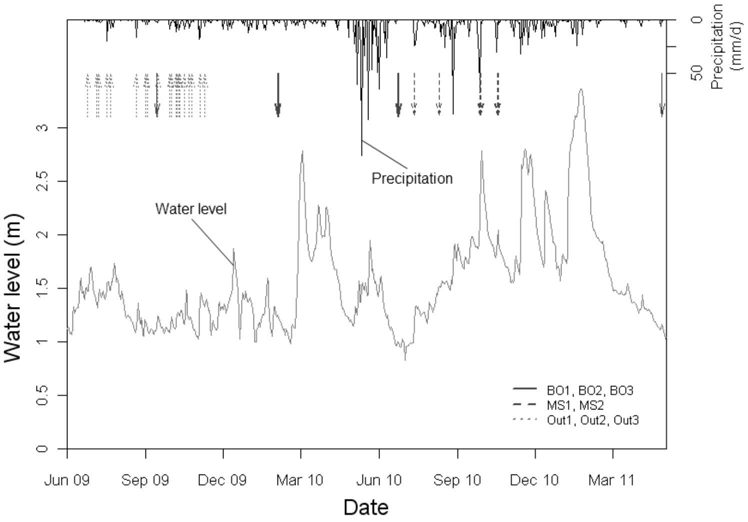


Figure 3.2: Sampling of sources and receptors, precipitation and Bode water level at the state gauge Staßfurt.

3.2.2 Chemical analysis

The samples were analyzed for As, the metals Al, Co, Cr, Cu, Fe, Pb, Zn, Ti and V, organic carbon (OC), inorganic carbon (IC), phosphorus (P) and nitrogen (N). The procedures were as follows: The sediment samples were dried at 55°C and sieved. The <63 µm fraction was analyzed for elements after microwave digestion with aqua regia using mass spectrometry with inductive coupled plasma (Agilent 7500c, Agilent Technologies, Santa Clara, CA, USA). Carbon and nitrogen were analyzed by infrared digestion after controlled combustion (Elementar vario El Cube, Elementar Analysensysteme, Hanau, Germany). Phosphorus contents were determined photometricly (CADAS200, Hach Lange, Düsseldorf, Germany) after combustion at 550°C adding of NH_4NO_3 and digestion with HCl.

The water samples were analyzed for dry weight suspended solids (SS) in accordance with German Industrial standards (DIN 38409-2). Metals were determined after microwave digestion with HNO_3/H_2O_2 as total content and after filtration (<0.45 µm) as dissolved fraction using mass spectrometry with inductive coupled plasma (Agilent 7500c, Agilent Technologies, Santa Clara, CA, USA). Organic and inorganic carbon was determined as total concentration and after filtration as dissolved fraction using a carbon analyzer (Dimatoc2000, Dimatech, Essen, Germany). Total nitrogen, ammonia, nitrate and nitrite and soluble phosphorus were determined using continuous flow analysis (Skalar, Breda, The Netherlands). Total phosphorus was determined using a photometer (CADAS200, Hach Lange, Düsseldorf, Germany). The particle-associated contents were calculated as the difference between total and dissolved concentrations divided by SS contents.

3.2.3 Data analysis

Principal Component Analysis (PCA)

Data analysis was carried out in the statistical environment R 2.12.0 (R Development Core Team 2009). We conducted a principal component analysis (PCA) based on singular value decomposition using the R package FatoMineR (Husson et al. 2010) to delineate sources and receptors. The data set included bed sediment, suspended sediment and urban wet weather particulate matter (PM) samples. The data were transformed and scaled to receive normal distribution of the parameters with a mean of 0 and a standard deviation of 1. IC, OC, N, Al, As, Co, Cr, Cu, V and Zn were log transformed, Fe, Pb and Ti were square root transformed. Elements such as P, Cd and Ni were excluded from the PCA because more than 10% of the data were below the limit of quantification or not available.

Multivariate mixing model

To quantify the contribution of urban areas to the sediment trap fines, we used a multivariate mixing model approach (Friedlander 1973; Collins et al. 1997; Collins et al. 2010). It assumes that linear mixing of sources determines the receptor contents according to equation 3.1

$$c_i = \sum c_{ij} a_j \qquad (3.1)$$

where c_i is the receptor content of element i, c_{ij} the content of element i of source j and a_j the contribution of source j under the constraints that the source contributions are at least 0 and sum up to 1.

As sources we considered urban wet weather PM as proxy for urban areas, fines from bed sediment cores as proxy of the local background and suspended sediment which resembles the upstream land use of the river catchment. The characterisation of these sources is given in Table 3.1.

Table 3.1: Description of the source samples by the 10th, 50th and 90th percentile of particle-bound contents of major constituents.

		Bed sediment core (Bed sed)			Suspended sediment (Sus sed)			Urban wet weather PM (Urban PM)		
		n = 9			n = 53 (14 low flow grab samples), i = 5, E = 5			n = 116, i = 3, E = 39		
		P10	P50	P90	P10	P50	P90	P10	P50	P90
IC	mg kg^{-1}	2600	4700	6000	<5300*	2600	10500	200	2000	5400
OC	mg kg^{-1}	17500	22500	29600	13000	35000	97000	20000	112000	240000
P	mg kg^{-1}	1000	1100	1500	2200	3900	6100	<2000*	5200	8200
N	mg kg^{-1}	1700	2200	2500	9000	42000	100000	8200	35000	48000
Al	mg kg^{-1}	6300	19100	20900	3200	20100	41800	12500	20800	33600
As	mg kg^{-1}	8,9	13	17	<5.1*	24	120	2,3	5,8	10
Cd	mg kg^{-1}	0,6	1,1	1,5	<4.8*	<8.3*	<19*	<0.2*	<0.7*	1,1
Co	mg kg^{-1}	10	12	16	<3.8*	15	38	4	8,2	12
Cr	mg kg^{-1}	39	43	56	32	67	140	18	40	66
Cu	mg kg^{-1}	36	47	65	36	140	360	280	470	640
Fe	mg kg^{-1}	23300	26700	29100	10500	37500	58600	8600	19600	30100
Ni	mg kg^{-1}	32	35	42	42	63	200	22	26	30
Pb	mg kg^{-1}	47	64	90	120	150	220	47	76	134
Ti	mg kg^{-1}	820	1300	1500	74	690	1300	180	490	860
V	mg kg^{-1}	34	41	44	26	52	88	16	36	57
Zn	mg kg^{-1}	230	260	320	240	510	1100	940	1400	2400

* denotes limit of quantification, n is the ample size, i is the amount of sample sites and E is the amount of sampled urban wet weather or high flow events

The source contribution was calculated for bed sediment traps at the receptor sites BO1, BO2 and BO3. The characterization of these receptor sites is given in Table 3.2.

Table 3.2: Description of the receptor sites by the 10th, 50th and 90th percentile of particle-bound contents of major constituents.

		BO1.T			BO2.T			BO3.T		
		n = 15			n = 20			n = 12		
		P10	P50	P90	P10	P50	P90	P10	P50	P90
IC	mg kg^{-1}	5500	6300	9000	4800	6900	8600	19600	29800	39400
OC	mg kg^{-1}	31900	36700	46200	28900	36300	54100	23300	31800	46800
P	mg kg^{-1}	1500	1700	2100	1400	1700	2600	1500	2000	2600
N	mg kg^{-1}	3200	3700	5500	2700	3600	5800	2400	3200	5200
Al	mg kg^{-1}	6900	17500	21100	5600	18400	21500	4400	16200	17000
As	mg kg^{-1}	9.1	12	21	9.0	15	28	10	12	29
Cd	mg kg^{-1}	1.1	1.4	1.8	1.3	1.6	2.0	1.0	1.2	1.5
Co	mg kg^{-1}	10	11	15	9.5	11	14	7.1	8.7	9.2
Cr	mg kg^{-1}	34	40	82	38	52	181	46	64	137
Cu	mg kg^{-1}	40	53	65	36	53	64	42	52	61
Fe	mg kg^{-1}	21500	25300	27900	18900	24000	27700	18300	22200	23300
Ni	mg kg^{-1}	23	31	34	24	35	43	21	25	28
Pb	mg kg^{-1}	61	78	100	68	100	130	84	120	170
Ti	mg kg^{-1}	820	900	1100	750	880	1100	560	680	1000
V	mg kg^{-1}	33	36	41	30	37	42	29	35	37
Zn	mg kg^{-1}	250	310	430	230	310	360	180	200	260

* denotes limit of quantification, n is the sample size

The elements which determine the composite fingerprints were chosen by a two-step procedure. It was checked whether the element contents of the receptor were in the range of the element contents of the sources (Collins et al. 2010). This constraint has to be met under the assumption that all relevant sources are considered. It was not met by Cr at BO1, and by IC, V and Zn at BO3. Additionally Cd was excluded from the calculation because its contents were often below the limit of quantification. Second we selected the combination of elements which distinguish the sources. Therefore we applied a Kruskal-Wallis-Test to test whether the elements are different among the sources (Collins and Walling 2002). All elements passed this test ($p<0.05$).

The system of linear equations was solved by linear regression and minimization of weighted least-squares. Therefore we log-transformed the data to fulfil the mathematical requirement of normal distribution and homoscedasticity. We decided that the element weights should reflect how well the element content was predicted by the mixing model. The elements are thus weighted according to their susceptibility to biogeochemical processes as suggested by Collins et al. (1998). The weights were therefore iteratively corrected to the coefficient of determination (COD) multiplied by 10 to have weights larger than 0 until the COD of the elements changed by less than 1%. As coefficient of determination (COD), we used Pearson's correlation coefficient between measured and predicted contents. A weight below 0 was adjusted to 0.01 (Table 3.3). In some studies the contents were corrected for differences in particle size, organic matter content and the conservativeness of elements (Collins et al. 1997; Motha et al. 2003; Fox and Papanicolaou 2008). We refrained from doing so because the particle size changes especially during erosion processes. As the sources are sampled close to the receiving sites, we expect the particles to change little in size. Furthermore the element weights take biogeochemical processes into account.

Table 3.3: Weights of the elements for the mixing models at the three receptor sites BO1, BO2 and BO3.

	IC	OC	P	N	As	Co	Cr	Cu	Fe	Ni	Pb	Ti	V	Zn
BO1	7.43	6.58	8.50	0.01*	0.01*	2.14	-	8.07	0.01*	0.01*	8.80	5.15	1.45	8.46
BO2	4.09	0.01*	6.90	8.45	7.70	6.97	5.37	0.01*	6.82	7.12	6.59	3.60	6.00	0.01*
BO3	-	8.33	8.68	4.27	0.01*	0.01*	7.80	0.11	0.01*	0.74	7.52	9.04	-	-

* denotes the weight was adjusted to 0.01 because the COD was negative

We repeated the calculation 1'000 times. Thereby we considered the variability in the source profiles by Latin hypercube sampling from the parameters' distributions. Correlation between the parameters was taken into account.

With the source contribution a_j we calculated the source contribution to single element contents a_{ij} by

$$a_{ij}=c_{ij}a_j/c_i \tag{3.2}$$

3.2.4 Validation

The results are assessed by comparing the measured and the predicted element contents by calculating Pearson's correlation coefficient. We also performed a sensitivity analysis by excluding each of the elements from the mixing model. This procedure reveals how much each element of the multivariate mixing model affects the calculation. It also shows how much the calculation may be biased by the selection of parameters.

The uncertainty of the results was additionally assessed by repeating the mixing model calculation on literature data about the geochemical background of the Bode River stretch instead of the sediment core samples at BO1 as source (Furrer 2000). The data are the mean values from two sites (Table 3.4). One site is situated approximately 20 river km upstream of BO1, the second site is situated 2 km downstream of BO2. Cu was excluded from the calculation at all sampling sites; Ti was excluded from the calculation at BO1 and V at BO3. These elements were part of the initial multivariate mixing model. Compared to the geochemical background, the bed sediment core samples, which serve as source in the initial mixing model, are enriched in Ti by a factor of 1.4 and depleted in Cu and V by a factor of 0.9 and 0.6, respectively. Cd was also excluded from the calculation because the Cd content of the suspended sediment was often below the limit of quantification as mentioned above.

Table 3.4: Characterization of the geochemical background of the Bode river close to Staßfurt in mg kg^{-1} (Furrer 2000).

C	N	As	Cd	Co	Cr	Cu	Fe	Ni	Pb	Ti	V	Zn
18500	2100	12	0.3	12	65	54	40900	43	43	900	73	170

3.3 Results

3.3.1 Source identification

The principal component analysis (PCA) reveals whether the considered sources may be delineated. It further identifies key elements determining the source specific fingerprints. Three components have eigenvalues > 1 and are thus presented (Figure 3.3a and b). The PCA indicates that it is reasonable to consider bed sediment, urban wet weather PM and suspended sediment as sources of fines captured by bed sediment traps.

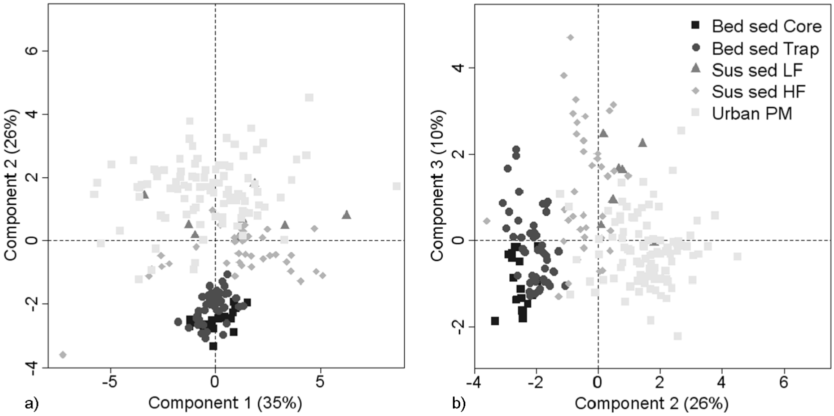


Figure 3.3: Score plots of PCA for particle bound contents of fines in bed sediment traps (Bed sed Trap), bed sediment cores (Bed sed Core), suspended sediment during low flow (Sus sed LF), suspended sediment during elevated flow (Sus sed HF) and urban wet weather particulate matter (Urban PM); component 1 and component 2 (a), component 2 and component 3 (b).

The first component does not delineate the sample types. It is most heavily loaded with Fe, Ti, V and Al (Table 3.5). The second component separates bed sediment and urban wet weather PM. It is most heavily loaded with Cu, Zn, N and OC. In this dimension the suspended sediment ranges between the bed sediment and the urban wet weather PM. Thereby the suspended sediment samples taken during high flow conditions (HF) are situated close to bed sediment samples whereas suspended sediment samples taken during low flow conditions (LF) are aligned close to urban wet weather PM samples.

Table 3.5: Component coordinates and eigenvalues of considered components (Parameters of maximum loading are bold).

	Component 1	**Component 2**	**Component 3**
IC	0.15	0.51	**0.61**
OC	-0.10	**0.65**	-0.23
N	0.14	**0.79**	0.39
Al	**0.72**	0.44	-0.40
As	0.48	-0.38	0.23
Co	0.71	-0.22	-0.17
Cr	0.63	-0.35	0.25
Cu	0.19	**0.86**	-0.14
Fe	**0.90**	-0.07	-0.09
Pb	0.69	-0.06	0.52
Ti	**0.77**	-0.27	-0.38
V	**0.89**	0.05	0.06
Zn	0.27	**0.86**	-0.13
Eigenvalue	***4.49***	***3.38***	***1.34***

The third component delineates the suspended sediment from the other sample types. This is explained by IC. Especially suspended sediment downstream of BO2 is enriched in IC.

The PCA does not only reveal that the sources are delineated by the considered elements. It further suggests that the bed sediment traps receive fines from urban wet weather PM, suspended sediment and bed sediment cores. Regarding the second and third component, the samples of the bed sediment traps range among these three sources.

3.3.2 Source contribution

Source contribution to fine sediment

The fines captured by the bed sediment traps mainly originate from bed sediment and thus from the local surrounding of the traps. Urban wet weather contributes approximately 10 to 15% of the fines at the three sampling sites BO1, BO2 and BO3 (Figure 3.4). It is obvious that the Bode River upstream of Staßfurt at BO1 is already influenced by urban areas. The intrusion of fines from urban wet weather increases from BO1 to BO2 but decreases at site BO3. Regarding suspended sediment, though, there is a downstream gradient so that the intrusion of suspended sediment increases from 5 to 20% between BO1 and BO3. Especially at sampling site BO3, the source contributions are more variable than at BO1. This indicates that effluent plumes may not be mixed in entirely at these sites.

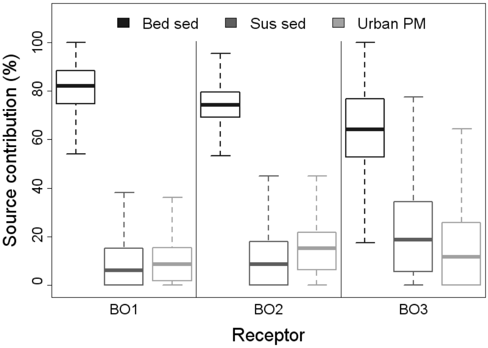


Figure 3.4: Source contribution to fines captured by sediment traps at BO1, BO2 and BO3 (The median is shown as a broad bar, the boxes cover the interquartile range, and the whiskers extend to minimum and maximum values).

Source contribution to elements

Up to 15% of the fine sediment captured by the traps originate from urban wet weather PM. Due to the specific element patterns of the sources, the contribution to single element contents clearly exceeds 15%. Hence up to 40-60% of P, N, Cu and Zn at the receptor sites originate from urban wet weather PM (Figure 3.5). By contrast the elements As, Cr, Co, Ni and Pb mainly originate from bed sediment. Suspended sediment is a major source of N at each receptor site and a major source of all considered elements at site BO3. In contrast to the other elements, bed sediment contributes only about 20% of N and is thus a negligible source of N.

The variability of the source contribution is high. Especially those elements for which urban wet weather PM and suspended sediment are important sources exhibit a high interquartile range between 5 and up to 70%.

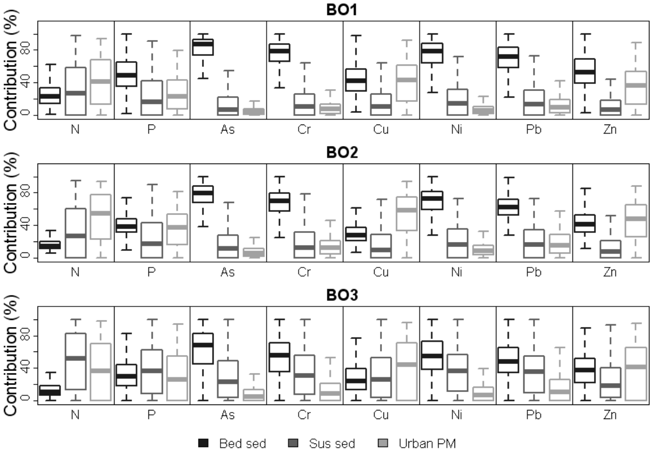


Figure 3.5: Source contribution to the pollutants of fines captured by sediment traps (The median is shown as a broad bar, the boxes cover the interquartile range, and the whiskers extend to minimum and maximum values).

3.3.3 Validation

Most elements are well predicted by the mixing model with an overall COD of 0.90. The predicted N contents deviate most from the measured contents and are systematically overestimated by the mixing model at all sampling sites (Figure 3.6). N though has a high COD of at least 0.85 at sampling site BO2 (the weights divided by 10 in Table 3.3 correspond to the COD). P and Pb exhibit high COD and are well predicted at all three sites. The COD of the other elements deviate among the receptor sites. IC, Cu and Zn are well predicted at BO1. At BO2 and BO3, Cu and Zn are overestimated whereas IC contents are under-predicted at BO3 by the mixing model.

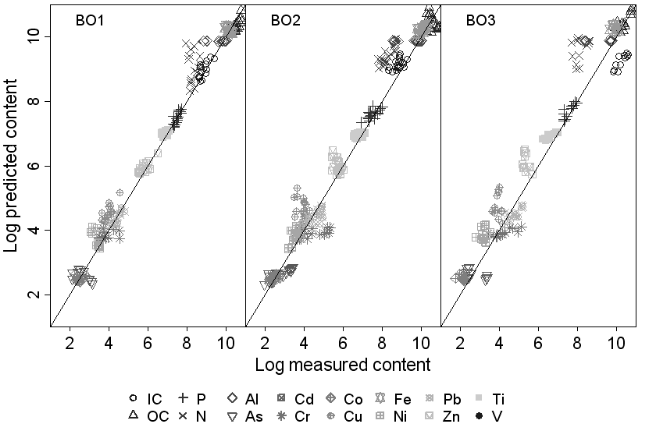


Figure 3.6: Measured versus predicted contents for each of the considered element at the receptor sites BO1, BO2 and BO3.

The impact of the elements on the calculation was assessed by excluding each of the elements from the mixing model. This changes the median contribution of urban wet weather PM at most by 100% (Table 3.6). At sampling site BO1 Cu and Ti influence the calculation most, at BO3 Pb and Ti have the highest impact. The mixing model of BO2 is less sensitive than the mixing models of BO1 and BO3. Excluding As from the calculation at BO2 increases the median contribution of urban wet weather PM only by 33%.

Table 3.6: Change of contribution of urban wet weather PM (%) to fines in sediment traps at the sites BO1, BO2 and BO3 when excluding the respective constituent from the calculation.

	IC	OC	P	N	As	Co	Cr	Cu	Fe	Ni	Pb	Ti	V	Zn
BO1	-2	-4	-2	0	0	-4	-	76	0	0	3	-85	-6	23
BO2	-1	0	-8	23	33	-12	8	0	-10	-10	6	-11	-10	0
BO3	-	-30	-17	38	0	0	35	1	0	-13	53	-100	-	-

Considering the geochemical background alters the results (Table 3.7). Compared to the initial mixing model, urban wet weather PM is a more relevant source of fine sediment and contributes up to 25%. Thereby the bed sediment core samples, which serve as source in our initial mixing model, are already influenced by urban areas. About 15% of the fines of the bed sediment core samples originate from urban wet weather PM. In contrast to the initial mixing model, sampling site BO2 is least influenced by urban wet weather PM.

Table 3.7: The 10th, 50th and 90th percentile of the contribution (%) of geochemical background (Geo back), suspended sediment (Sus sed) and urban wet weather PM (Urban PM) to fines in bed sediment cores (Bed sed) and bed sediment traps at BO1, BO2 and BO3 based on literature geochemical background data.

	Bed sed			**BO1**			**BO2**			**BO3**		
	P10	P50	P90	P10	P50	P90	P10	P50	P90	P10	P50	P90
Geo back	61	73	86	50	63	72	51	64	77	43	62	75
Sus sed	0	5	31	0	9	41	0	15	41	0	9	43
Urban PM	0	16	32	1	24	41	0	17	36	3	24	43

3.4 Discussion

3.4.1 Source identification

In our study urban wet weather PM is characterized by elevated Cu and Zn contents. These metals are typical for urban areas (Viers et al. 2009). Additionally urban wet weather PM exhibits elevated N and OC contents which are related to wastewater.

We considered suspended sediment as possible source that is representative for the upstream river catchment. The PCA shows that suspended sediment is separated from bed sediment and urban wet weather PM by elevated IC contents. These originate from the discharge of a sodium carbonate production site upstream of BO3. Suspended sediment further exhibits a composite fingerprint which is close to the urban wet weather PM during low flow conditions because the upstream catchment comprises urban areas such as the Towns of Halberstadt, Quedlinburg and Oschersleben with populations of between 20’000 and 40’000. During high flow the element pattern of suspended sediment is similar to the pattern of bed sediment. Such behaviour was also described for the Po River (Davide et al. 2003). The reason is that less polluted interstitial fines are remobilized during elevated flow.

The PCA results in a first component that does not delineate the sample types and is most heavily loaded with Fe, V and Al. Fe and Al are typical proxies for terrestic sources (Zoller et al. 1974; Sinex et al. 1981). But Fe and V differentiate among the sources so that these elements were part of the composite fingerprint.

3.4.2 Source contribution to fine sediment

The median contribution of urban wet weather PM to fine sediment of the traps is about 10-15%. We address how valid this result is. Three aspects are of concern regarding mixing models of composite fingerprints: the capture of all relevant sources, the neglect of biogeochemical processes and the setup of the multivariate mixing model, i.e. the selection of parameters and their impact on the calculation.

An example for a non- or rather inappropriately captured source during our field study is the discharge of the sodium carbonate production site downstream of BO2. It influenced the suspended sediment samples taken at MS2 which are thus characterized by high IC contents.

Since the IC contents at BO3 still exceed those of the suspended sediment, we had to exclude IC from the mixing model. Without IC the source suspended sediment was less distinct from the other two sources. We could run the calculations, though, and the mixing model performed well reaching a COD of 0.84. Dilution by the missing source may explain why Co, Fe, Ni and Zn have lower contents at BO3 than at the receptor sites BO1 and BO2. But it is also possible that remobilization decreases the element contents at BO3. To explain the behaviour of the elements, it would be necessary to analyze the binding of the elements by sequential extraction (Ure et al. 1993, Kim et al. 2010, Yuan et al. 2011).

We expect that the reproducibility of the elements is governed by their susceptibility to biogeochemical processes. The COD varies among the parameters and sites. Only P and Pb have a high COD at all receptor sites. For the other elements, the COD does not exhibit a clear pattern among the sites. This suggests that the behaviour of the elements is locally determined. As the COD determines the weight of an element within the multivariate mixing model, the calculation is not biased by biogeochemical processes.

The third aspect concerning the validity of multivariate mixing models is their setup. We used composite fingerprints comprising of nutrients and metals whereby the weight of the fingerprint constituents is based on their reproducibility. The sources can be delineated as shown by the PCA. But elements such as Cu and Zn, which characterize the source urban wet weather best, play a minor role in the multivariate mixing model due to their limited reproducibility. Other studies use a stepwise algorithm based on a multivariate discriminant analysis to construct a fingerprint without redundant information (Collins et al. 1997; Collins and Walling 2002). Our mixing model, however, reproduces the element contents at the receptor sites well with an overall COD of 0.90. Thereby it performs best at BO1 reaching a COD of 0.95 and poorest at BO3 with a COD of 0.84 because of the missing source. We assessed the impact of the elements on the calculation by excluding single elements from the mixing model. We found that changing the considered composite fingerprint changes the outcome up to 100%. This basically means that the median contribution of urban wet weather PM ranges from about 0% up to 20%. This is within the interquartile range of the initial multivariate mixing model.

The contribution of urban wet weather PM is similar at BO1, BO2 and BO3. Considering regional geochemical background data confirms that the bed sediment upstream of Staßfurt is already influenced by upstream urban areas. Interestingly the bed sediment cores contain less urban wet weather PM and less suspended sediment than the bed sediment traps. Obviously the traps do not resemble the behaviour of the surrounding bed sediment in our study area. The sediment traps are free of any fine sediment when they are installed. They thus serve as sink so that they promote the intrusion of urban wet weather PM and suspended sediment.

3.4.3 Source contribution to elements

Due to the specific element pattern of urban wet weather PM it contributes up to 40-60% of N, P, Cu and Zn bound to the fines of the sediment traps. The first question to address is whether this is relevant for the sediment quality. As the studied Bode River stretch is nutrient rich and characterized by an excessive growth of macrophytes, the input of N and P from urban areas is critical. Additionally, according to German national standards, the bed sediment exhibits critical contents of Zn at BO1, BO2 and BO3 (LAWA 1998). In contrast to Zn, the bed sediment does not exhibit critical Cu contents. Moreover the fine sediment captured by the traps is not enriched in Cu compared to the geochemical background.

The second question is whether the results appear reliable. The mixing model predicts P well so that the results are reliable. Considering N yields a different result. The mixing model systematically over-predicts the N content at all receptor sites. The question arises whether N behaves differently depending on its source. Indeed we expect that N bound to urban wet weather PM is more subject to N transformation than other sources due to its high N content. Similarly the mixing model overestimates the Zn contents at the receptor sites BO2 and BO3. Here we also expect that Zn bound to urban wet weather PM is more subject to remobilisation because it is more bound to easily available fractions in urban wet weather discharge (Hnatuková et al. 2009).

Other major pollutants such as As, Cr, Ni and Pb mainly originate from the bed sediment along with Fe and Al which are proxies for terrestrial sources (Zoller et al. 1974; Sinex et al. 1981). These elements are thus catchment borne.

A critical issue for assessing the relevance of urban wet weather as source of nutrients and pollutants is the variability. The contribution of urban wet weather PM to fine sediment exhibits a maximum interquartile range of 0 to 20%. When calculating the source contribution to single elements this variability increases because of the variability of the element content of the sources. Especially concerning N the contribution of urban wet weather PM is variable and reaches an interquartile range between 5 and 80% at BO3. However this reflects the intermittent character of the urban wet weather discharge activity and does by no means indicate uncertainty of the data analysis.

3.5 Conclusions

We quantified how much bed sediment, urban wet weather particulate matter (PM) and suspended sediment contribute to the fines and associated elements captured in sediment traps. For the calculation we used a multivariate mixing model of composite fingerprints. The main findings of our study are:

In our study area, it is possible to characterize the sources by nutrients and elements. This was shown by a principle component analysis.

In our study area, urban areas contribute approximately 10-15% of fine sediment which intruded into sediment traps. These sediment traps, though, overestimate the anthropogenic impact on the bed sediment.

Due to the specific element pattern of urban wet weather PM, which is enriched in Cu, Zn and N, urban areas are important sources of bed sediment pollution. However our mixing model overestimates the contribution of urban wet weather PM to N and Zn contents in the bed sediment because of transformation and remobilisation.

For the calculation of the source contribution, the consideration of all relevant sources and the description of the composite fingerprint are critical issues. Neglecting biogeochemical processes is of minor importance for the setup of mixing models, while they have to be taken into account when the source contribution to single pollutants such as N is calculated.

Especially concerning the variability of the source contribution to single elements, the source characterization should be improved. Our source samples have a high temporal resolution whereas the receptor samples exhibit a time-integrated signal. It would be reasonable to take time-integrated samples of the sources as well.

4 Impact of soda ash industry discharge on sediment-bound elements in a receiving water

4.1 Introduction

Soda ash industry discharges high loads of ammonia, chloride, calcium and sodium changing the water chemistry and the ecosystem assemblage (Effler et al. 1991; Hurteau et al. 2010; Jadeja and Tewari 2011). One aspect is that $CaCO_3$ precipitation increases the particle load in receiving waters. The fine sediment is an important water quality measure. It influences the turbidity and hence the light conditions. Furthermore pollutants such as heavy metals may be associated with fine sediment. Consequently we expect that particles originating from soda ash production influence the binding of these pollutants and thus their bioavailability.

Source apportionment is a possibility to study how much soda ash production discharge contributes to fine sediment in streams. Such source apportionment is widely applied in air pollution and water quality studies (e.g. Hopke et al. 1976; Gaarenstroom et al. 1977; Pekey et al. 2004, Zhou et al. 2007). Thereby the main assumption is that the sources exhibit distinct patterns and that the mixing of the sources determines the pattern of the receiving site. In air and water pollution studies, it is common that sources are not well known or difficult to monitor. Hence, multivariate statistics is used to reveal the source patterns and contributions from data of the receiving sites. Multivariate statistics are appealing because no prior knowledge about the sources is required. Additionally, the source pattern may change between source and receiving site because of biogeochemical processes (Zoller et al. 1974; Reimann and de Caritat 2005). These effects are indirectly taken into account when deriving the source pattern from data of the receiving site. It may complicate the interpretation and identification of the source patterns, though.

Typical methods used in source apportionment are principal component analysis and factor analysis. Recent developments such as positive matrix factorization and multi curve resolution consider constraints such as non-negative source characterisation and contribution (Paatero and Tapper 1994; Tauler et al. 2009).

The element binding is also an important aspect when assessing the impact of soda ash industry discharge and other sources of pollution. The phase in which elements are bound influences the potential of remobilisation and thus the bioavailability. For that reason many studies on soil and sediment pollution do not only consider total concentrations but phase specific concentrations of inorganic pollutants (e.g. Tokalioglu et al. 2010). These are determined by sequential extraction schemes. Such a sequential extraction scheme was introduced by the European Community Bureau of Reference (BCR). It comprises of three steps. The first step leaches the acid soluble elements. These elements are adsorbed onto particle surfaces and incorporated into carbonates. The second step remobilises reducible elements which are bound to iron and manganese oxides and hydroxides. The third step extracts oxidisable elements which are incorporated into organic matter and sulphides. The remaining element contents are incorporated into crystalline structure and are acid soluble (Ure et al. 1993; Rauret et al. 1999).

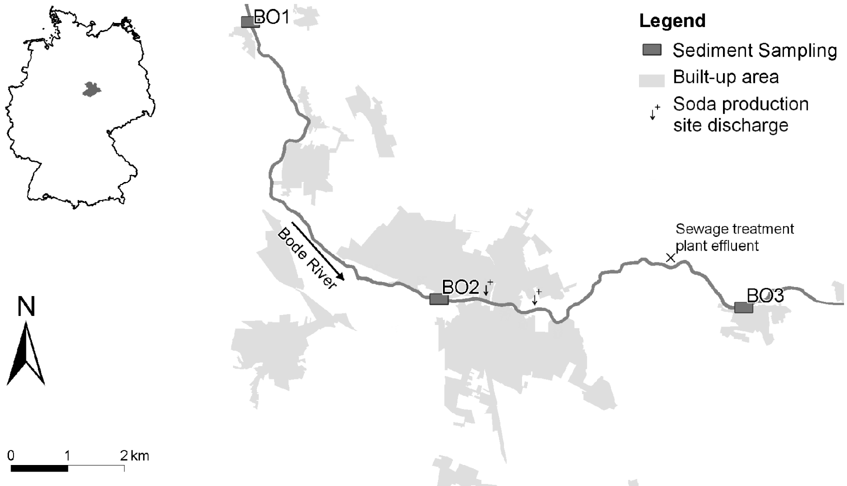
There is evidence that anthropogenic inputs of pollutants impact the binding pattern. Studies showed that background contamination is related to elements bound in the residual phase and thus exhibits a limited mobilisation potential. By contrast anthropogenic pollution increases the mobilisation potential as a higher percentage is bound to organic matter, iron and manganese oxides and hydroxides or adsorbed onto particle surfaces. Hence studies found that Cu and Zn are more easily available downstream of urban areas (Hnatuková et al. 2009; Priadi et al. 2011). Similarly metals are more mobile bound in street sediment compared to natural background (Stead-Dexter and Ward 2004; Zehetner et al. 2009). The impact of soda ash industry was not yet investigated.

This chapter addresses how much a soda ash industry discharge contributes to fine sediment in a stream and it investigates the impact on the binding of priority elements such as Cu and Zn. We use nonnegative matrix factorization to identify soda ash industry discharge and calculate its contribution to fine sediment load and element contamination. We further study the element binding on fine sediment in the receiving water by the BCR extraction scheme.

4.2 Materials and methods

4.2.1 Sampling campaign

The study area was the lower reach of the Bode River close to the Town of Staßfurt (Figure 4.1). The Bode River drains the Northern Harz mountain range and merges into the Saale River. It is a mid-sized fine to coarse substrate dominated siliceous highland river which has a mean discharge of 13.0 m^3/s in Staßfurt. Arable land covers in total 62% of the catchment. 21% of the catchment, especially in the Harz Mountains, are forest. The lower reach of the stream has a sandy to gritty sediment. It exhibits a moderate to poor ecological status (Minestry of Agriculture and the Environment of the State Saxony-Anhalt 2005). Due to former mining activities in the Harz, the Bode river and especially its tributary the Selke River is characterized by elevated metal concentrations such as Cu, Zn, As and Pb. Within Staßfurt a soda ash production site discharges into the Bode River.



Sources:
Geobasisdaten © Vermessungsverwaltungen der Bundesländer und BKG (www.bkg.bund.de)
Wasser- und Abwasserzweckverband "Bode-Wipper"

Figure 4.1: Location of the Bode Catchment and sampling sites.

We installed sediment traps at three sites in the Bode River to capture the intrusion of fines as described by Lisle (1989) and Sear (1993). A sediment trap consisted of a wire basket of a mesh size of 2-3 mm filled with sieved bed sediment. They were exposed for 3-10 months (Table 4.1). At two sites five sediment traps were installed, at one site four. To allow for a relatively easy lifting and exchange of the baskets, they were put into a second larger outer basket and a bag of nylon was stored underneath the trap.

Table 4.1: Dates of installation and exchange of sediment traps at sampling sites BO1, BO2 and BO3.

Sampling site	Installation	Exchange 1	Exchange 2	Exchange 3	Exchange 3
BO1	3 June 3 2009	14 Sep 2009	- (Ice cover)	24 June 2010	28 April 2011
BO2	4 June 2009	14 Sep 2009	2 Feb 2010	23 June 2010	28 April 2011
BO3	26 Aug 2009	-	3 Feb 2010	23 June 2010	28 April 2011

4.3 Analysis

The samples were analyzed for the alkali earths Ca, K, Mg, Na; As, B, the metals Al, Co, Cr, Cu, Fe, Pb, Zn, Ti, V, Ce, La, Nd, Pr, Sm, organic carbon (OC), inorganic carbon (IC), phosphorus (P) and nitrogen (N). The procedures were as follows: The sediment samples were dried at 55°C and sieved. The <63 µm phase was analyzed for elements after microwave digestion with aqua regia using mass spectrometry with inductive coupled plasma (Agilent 7500c, Agilent Technologies, USA). Carbon and nitrogen were analyzed by gas chromatography (Elementar vario El Cube, Elementaranalysensysteme, Germany). Phosphorus concentrations were determined photometricly (CADAS200, Hach Lange, Düsseldorf, Germany) after combustion at 550°C adding of NH_4NO_3 and digestion with HCl.

In addition to total contents, we applied the BCR extraction scheme to three samples at each site of the sampling event of 23/24 June 2010. The contents of the elements As, Cd, Cr, Cu, Ni, Pb, and Zn were determined to assess the potential of remobilisation and thus the bioavailability. We followed the sequential extraction procedure by Rauret et al. (1999). Step 1 extracts metals which are exchangeable and bound to carbonates. Therefore 0.11 mol/l acetic acid is added to 1 g dried sediment < 63 µm. The sample is shaken for 16 h and centrifuged. The extract is taken for analysis. The residue is washed with distilled water prior to step 2. To extract reducible elements, which are bound to iron and manganese oxides and hydroxides, 0.5 mol/l hydroxylammonium chloride is added to the sample. The sample is again shaken and centrifuged, and the extract is taken for analysis. In step 3 oxidisable elements, which are mainly bound to organic matter and sulphides, are extracted. Therefore 8.8 mol/l H_2O_2 is added and the sample is digested at room temperature for 1 h and at 85°C for 2 h prior to the addition of 1 mol/l ammonium acetate. The sample is then shaken and centrifuged. The extract is taken for analysis. The residual phase was determined by subtracting the sum of step 1 to 3 from the total content. The accuracy of the sequential extraction was checked by the Freshwater sediment

BCR 701. Recovery rates of 88 – 115% for step 1, 102 – 152% for step 2 and 41 – 72% for step 3 were found. The recovery for step 3 is only acceptable when samples are compared with one another and not with results from other studies.

4.4 Data analysis

We applied nonnegative matrix factorization (NMF) to the total content data to identify sources of fine sediment. Nonnegative matrix factorization decomposes the data matrix X ($m \times n$) of m elements in n samples into

$$X = WH \tag{4.1}$$

where W ($m \times p$) is the factor loading matrix and H ($p \times n$) the factor score matrix and p the number of considered sources. The NMF was carried out with the R-package NMFN (Liu 2009). Thereby initial values of W and H are randomly chosen and iteratively optimised by multiplicative updates. Negative entries in W and H are not allowed. The element contents were standardised. A critical issue is the number of considered sources. We applied a principle component analysis on the standardised data. Six components had an eigenvalue larger than 1. The number of considered sources was thus six. In total 47 samples (n) and 26 elements (m) were considered so that the following condition of Henry et al. (1984) for receptor modelling was fulfilled

$$n > 30 + \frac{m+3}{2} \tag{4.2}$$

The factor scores were considered to represent the source contribution a_{jk} to sample j of source k which was calculated by

$$a_{jk} = \frac{H_{jk}}{\sum_{k=1}^{p} H_{jk}} \tag{4.3}$$

The sources were characterized by linear regression of a_{jk} to the original data matrix as described by Thurston and Spengler (1985)

$$X_i = \sum_{k=1}^{p} C_{ik} a_{jk} \tag{4.4}$$

where X_i is the measured contents of element i and C_{ik} is the content of element i in source k. Except for OC, Al, Co, Fe, Ni, Pr, Ti and V, the element contents were log-transformed to be normally distributed. All data analysis was carried out in the statistical environment R 2.12.0 (R Development Core Team 2009).

To assess the source identification of the soda ash industry, we took a grab sample of sediment from the outlet of the soda ash production site on 22 February 2011 (Table 4.2). Total contents of the elements were determined as described in Section Analysis.

Table 4.2: Element contents (mg/kg) of a grab sample from sediment at the outlet of the soda ash production site.

Ca	**K**	**Mg**	**Na**	**IC**	**OC**	**N**	**P**	**Al**	**As**	**B**	**Cd**	**Ce**
202000	2290	2000	11200	62700	-	1300	600	2310	13	< 5*	3	10
Co	**Cr**	**Cu**	**Fe**	**La**	**Nd**	**Ni**	**Pb**	**Pr**	**Sm**	**Ti**	**V**	**Zn**
7.6	49	69	20600	4.3	7.3	24	233	1.7	2	59	14	308

4.5 Results and discussion

4.5.1 Element behaviour at the sampling sites

The element behaviour from sampling site BO1 to BO3 is shown in Table 4.3. The sampling sites BO1 and BO2 are similar. Only Cr and Pb contents increase by 30%. This enrichment, however, is not significant ($p<0.05$, resampling of the median contents 1000 times). From BO2 to BO3, the element contents change profoundly. Ca, Na and IC exhibit significantly higher contents at site BO3 than at BO2. IC contents increase most by a factor of almost 4. This indicates that $CaCO_3$ and Na_2CO_3, which originate from the soda ash production, are retained by the sediment traps (Effler et al. 1991; Hurteau et al. 2010). P, B, Cr and Pb are also enriched although not significantly. By contrast, the contents of Cd, Co, La, Nd, Ni and Zn are significantly lower than upstream of the soda ash production discharge.

Table 4.3: The 10th, 50th and 90th percentile of the element contents of fine sediment captured by traps at the sampling sites BO1, BO2 and BO3 (n denotes the sample size).

		BO1.T			**BO2.T**			**BO3.T**		
		n = 15			n = 20			n = 12		
		P10	P50	P90	P10	P50	P90	P10	P50	P90
Ca	mg kg^{-1}	19200	25900	27700	18800	25200	35600	62300	90300	119500
K	mg kg^{-1}	3000	4200	5800	3100	4000	5100	3400	3800	4300
Mg	mg kg^{-1}	4100	4700	5600	4000	4500	5600	3900	4000	4400
Na	mg kg^{-1}	500	600	800	500	600	800	800	1100	1400
IC	mg kg^{-1}	5500	6300	9000	4800	6900	8600	19600	29800	39400
OC	mg kg^{-1}	31900	36700	46200	28900	36300	54100	23300	31800	46800
P	mg kg^{-1}	1500	1700	2100	1400	1700	2600	1500	2000	2600
N	mg kg^{-1}	3200	3700	5500	2700	3600	5800	2400	3200	5200
Al	mg kg^{-1}	6900	17500	21100	5600	18400	21500	4400	16200	17000
As	mg kg^{-1}	9.1	12	21	9.0	15	28	10	12	29
B	mg kg^{-1}	18	33	68	22	37	67	40	66	180
Cd	mg kg^{-1}	1.1	1.4	1.8	1.3	1.6	2.0	1.0	1.2	1.5
Ce	mg kg^{-1}	26	44	54	32	42	47	28	34	44
Cr	mg kg^{-1}	34	40	82	38	52	181	46	64	137
Co	mg kg^{-1}	10	11	15	9.5	11	14	7.1	8.7	9.2
Cu	mg kg^{-1}	40	53	65	36	53	64	42	52	61
Fe	mg kg^{-1}	21500	25300	27900	18900	24000	27700	18300	22200	23300
La	mg kg^{-1}	15	23	26	19	24	25	14	20	23
Nd	mg kg^{-1}	13	20	24	15	21	22	12	18	21
Ni	mg kg^{-1}	23	31	34	24	35	43	21	25	28
Pb	mg kg^{-1}	61	78	100	68	100	130	84	120	170
Pr	mg kg^{-1}	3.0	5.1	6.2	4.0	5.2	5.7	3.3	4.5	5.4
Sm	mg kg^{-1}	2.4	3.8	4.4	2.9	3.9	4.2	2.2	3.3	3.9
Ti	mg kg^{-1}	820	900	1100	750	880	1100	560	680	1000
V	mg kg^{-1}	33	36	41	30	37	42	29	35	37
Zn	mg kg^{-1}	250	310	430	230	310	360	180	200	260

Comparing the data with average element contents for the continental shale (Turekian and Wedepohl 1961) suggest that the study area is characterized by anthropogenic impact. Zn, Pb and Cd are more than 3 times higher in our study area. By contrast, rare earth metals are impoverished by a factor of about 0.5. Downstream of the soda ash discharge, Ca is enriched by a factor of 4. This already indicates that the soda ash industry influences the fine sediment at sampling site BO3.

4.5.2 Source characterisation and identification

The nonnegative matrix factorization (NMF) resulted in six distinct sources (Table 4.4). Source 2 is related to soda ash production discharge. The measured and predicted values have a Pearson's correlation coefficient of 0.99. The very high IC and Ca contents of the sediment in the soda ash industry outlet are well predicted by the NMF. The elevated Pb contents are also well predicted. The contents of other priority elements deviate up to a factor of 2. Hence the NMF overestimates the Cr content by 100% whereas Zn is underestimated by 65%. The Na content deviates most between measured and predicted source because Na is remobilized between the point of discharge and sampling site BO3. For this reason Na is only enriched by a factor of 2 between sampling site BO2 and BO3 whereas Ca is enriched by a factor of 4.

Source 3 most likely reflects the background contamination. It exhibits the highest contents of rare earth elements and K. It further exhibits the lowest contents of the priority elements As, Cr and Ni. The contents agree well with geological background contamination close to sampling site BO3 (Furrer 2000).

Sources 4 and 5 are likely to be sewage treatment plant and urban wet weather effluent. Thereby Source 4 is characterized by high OC, N and P contents. Considering these elements, Source 4 is most likely related to wastewater. It also exhibits high contents of Al, Fe, Cu and Zn. Such high metal contents were observed in urban wet weather discharge from the Town of Staßfurt (David et al. 2011). Source 5 has a high B content. Dissolved B is used as tracer for wastewater (Vengosh et al. 1994; Schreiber and Mitch 2006). The dissolved B is bound to sediment by coprecipitation and sorption to clay and Al- and Fe hydroxides (Parks and Edwards 2005).

Table 4.4: Factor loadings and calculated element contents of the NMF source (Contents which NMF loadings > 1 are bold).

	Content (mg/g)					
	Source 1	Source 2	Source 3	Source 4	Source 5	Source 6
Ca	40200	**170000**	18200	16900	31800	13900
K	4100	4000	**7700**	3200	2200	4200
Mg	**8700**	3900	7500	3100	2900	4200
Na	870	**1700**	580	450	810	360
IC	7800	**54700**	4600	6400	10900	3100
OC	37900	27600	25500	**84900**	16300	33900
P	1600	2300	1500	3300	1000	1900
N	5400	3300	2600	**9800**	2300	2900
Al	28300	6300	3200	**40300**	31100	8700
As	30	20	6	**50**	6	20
B	80	1	1	180	**180**	1
Cd	2	1	2	1	1	2
Ce	30	30	**70**	30	60	40
Co	10	3	10	20	8	20
Cr	40	100	30	30	60	**410**
Cu	**90**	40	40	100	50	40
Fe	29600	14600	19300	**36400**	20700	24700
La	10	10	**40**	10	30	20
Nd	10	10	**40**	10	30	20
Ni	40	20	10	30	30	**80**
Pb	80	**190**	110	70	40	190
Pr	2	3	**8**	3	7	5
Sm	2	2	**7**	2	5	4
Ti	720	320	1100	1200	1400	540
V	30	20	30	**50**	30	40
Zn	470	110	300	500	210	350

Source 6 is the most important source of Cr and Ni. These elements are important components of alloys. Within the Bode Catchment there are several metal casting manufacturers. One of them is situated in Staßfurt. The elevated Cr and Ni contents are probably historical because, nowadays, the metal casting manufacturer discharges its production wastewater to the sewage treatment plant.

Source 1 is difficult to interpret. It is most heavily loaded with Mg and Cu. But it also contains relative high contents of other elements so that Source 1 may not be identified.

The NMF shows that the study area is highly influenced by anthropogenic activities in the catchment (Table 4.5). Hence, only up to 30% of the fine sediment corresponds to natural fine sediment (Source 4). Within the studied river stretch, discharge from soda ash production (Source 2) becomes the most important anthropogenic source. Soda ash production site effluent is not clearly identified and comprises another source. This explains why Source 2 already contributes about 10% to fine sediment captured upstream of the soda ash production discharge. Even if this is taken into account, about 35% of the fine sediment at sampling site BO3 originate from soda ash production effluent. In addition to Source 2, Source 5 gains relevance throughout the study site because of sewage treatment plant discharge.

Table 4.5: Mean contribution (%) of the NMF sources to fine sediment at the sampling sites BO1, BO2 and BO3.

	Source 1	Source 2	Source 3	Source 4	Source 5	Source 6
BO1	17	9	26	22	17	9
BO2	15	11	24	18	15	16
BO3	5	45	13	14	19	5

4.5.3 Element binding

To assess the impact of the soda ash industry discharge on the receiving water quality, we further considered the binding of priority elements for samples taken on 23/24 July 2010 (Figure 4.2). In general the priority elements are mainly bound in the reducible phase (Phase 2) or in the residual phase (Phase 4). Only Ni, Cd and Zn have a considerable percentage bound in the most mobile phase (Phase 1). The oxidisable phase (Phase 3) only plays a role in binding Cr but not for any other priority element.

Between sampling site BO1 and BO2, the mobility of all priority elements increases because they are enriched in the easy extractable and carbonate bound phase (Phase 1). Simultaneously, most elements are impoverished in the residual phase (Phase 4). Such behaviour is explained by the impact of urban areas through urban wet weather flow (Hnatuková et al. 2009; Priadi et al. 2011).

Downstream of BO2 the element mobility is reduced. The contents of most priority elements in Phase 1 decrease between 25 and 50% from sampling site BO2 to BO3. This effect is caused by dilution. Soda ash production effluent yields carbonates and provides more than 70% of inorganic carbon (IC) at sampling site BO3. The reduction of the priority elements falls short of 70% which indicates that the soda ash production effluent also contains particle bound elements. This is also evident from the NMF results and the grab sample taken from the soda ash industry outlet.

The element contents in the other, less mobile, phases are less influenced by effluent from the soda ash production site. Only Cd, Ni and Zn which have a considerable percentage bound in the most mobile phase exhibit a significantly impoverished total content downstream of the outlet. Furthermore the total contents of Pb and Cr increase from BO2 to BO3 which is mainly explained by enrichment in Phase 2. It is thus not related to the soda ash industry discharge. Unfortunately the NMF reproduces the enrichment, especially of Cr, at sampling point BO3 poorly so that we cannot explain this element behaviour.

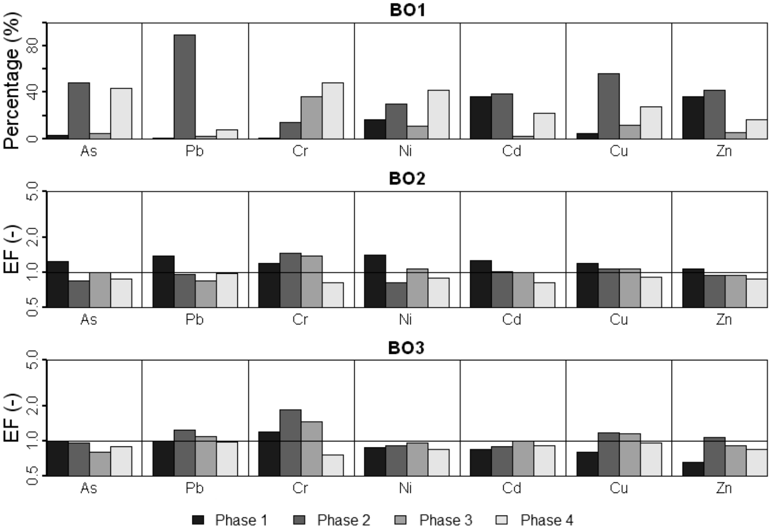


Figure 4.2: Binding of elements at the sampling site BO1 based on BCR extraction and enrichment factors (EF) of BCR phases at BO2 and BO3 compared to BO1.

4.6 Conclusions

This chapter addresses how much a soda ash industry discharge contributes to fine sediment and how it influences the binding of priority elements such as Cu and Zn in a receiving river. We used nonnegative matrix factorization to identify soda ash industry discharge and calculate its contribution to fine sediment load. Main findings of the study are:

Nonnegative matrix factorization (NMF) is able to identify soda ash industry effluent as source of fine sediment in our study area. This allows to calculate the source contribution.

Soda ash industry discharge is a major source of fine sediment in our study area. It increases the fine sediment load by about 35% and has to be considered in sediment management schemes.

Particles originating from soda ash production exhibit low contents of priority elements compared to other anthropogenic sources such as urban wet weather discharge. This reduces most element contents downstream of the outlet due to dilution.

Soda ash industry effluent mainly contains insoluble carbonates so that priority elements are diluted in the most mobile phase. Consequently the bioavailability of the priority elements decreases due to the effluent from the soda ash production site.

5 Summary and conclusions

The aim of this work was to study how much urban areas contribute to fine sediment in a receiving water body. It thereby emphasized on the intrusion of fine sediment in the hyporheic zone because the hyporheic zone is an important stream habitat. The fate of particulate matter emissions was studied by two different source apportionment methods based on sediment-associated element patterns. Successful source apportionment is necessary to assess the deteriorating effects of particulate matter emissions from urban areas.

In chapter 2, the particle associated element patterns of three urban wet weather outlets of the Town of Staßfurt were investigated. These element patterns are in general determined by the sources of the elements. However, catchment complexity exacerbates the apportionment of element sources because of interactions with the sewer sediment and superimposed discharge from subcatchments. These processes also cause relatively high within-site variability which is as high as the variability between sampling sites.

The different points of urban wet weather discharge, however, may not be delineated from one another in the receiving water. In fact, urban wet weather discharge has to be seen as nonpoint source because the source specific patterns are blurred within the receiving water body. At least particulate matter from urban areas is different from river borne fine sediment by elevated contents of e.g. nitrogen, phosphorus, copper and zinc, as shown in chapter 3.

In the study area, roughly 10% of the fine sediment captured by sediment traps originate from urban areas. Because of elevated contents of e.g. zinc, urban areas contribute up to 40% of the sediment-bound element load. Interestingly, the Town of Staßfurt has no significant impact on the composition of the fine sediment so that upstream of Staßfurt as much fine sediment originates from urban areas as downstream of Staßfurt. Consequently, most particles retarded by the sediment traps originate from upstream urban areas. This indicates that the transport of suspended sediment and thus particulate matter from urban areas is the major process compared to retention in interstices. Sediment balance studies have come to similar conclusions (e.g. Lambert and Walling 1988; Cushing et al. 1993).

A focus of chapter 3 was the uncertainty induced by biogeochemical processes. For source apportionment of fine sediment, biogeochemical processes are of minor relevance. But concerning the sources of element loads, biogeochemical processes should be considered. It was revealed that the multivariate mixing model over-estimated the nitrogen and, to a lesser extent, the zinc contents. This indicates that nitrogen and zinc are prone to remobilization and transformation.

The sediment traps do not mimic the bed sediment dynamics very well and rather serve as sink so that the intrusion of particulate matter from urban areas is over-estimated. To better mimic the bed sediment behaviour, the exposition of the sediment traps should depend on stream characteristics. In our case, the sediment traps should have been exposed longer. At least, this finding suggests that the Bode River is not subject to scouring due to altered geomorphology and altered flow regime.

In chapter 4, the multivariate receptor model indicates that the fine sediment of the Bode River at the Town of Staßfurt is highly influenced by anthropogenic activities which contribute up to 70% of the fine sediment. Besides urban wet weather discharge, mining activities play a role. Downstream of the Town of Staßfurt, the soda ash production increases the fine sediment load significantly. By contrast, the multivariate fingerprinting approach (chapter 2) considering geological background contamination suggests that anthropogenic sources contribute roughly 45% of the fine sediment and this contribution does not change significantly from up- to downstream of Staßfurt. Thereby the soda ash production site was neglected. This highlights that the source apportionment approaches are sensitive to the consideration and characterization of possible sources.

An issue of multivariate fingerprinting (chapter 2) is that the behaviour of some elements is not reproducible because sources may not be known. In this study, inorganic carbon and chromium were such cases. Multivariate receptor models do not have this drawback. Inorganic carbon is well explained by the soda ash production effluent which was neglected as source in the calculations of chapter 2. But the interpretation of the chromium behaviour remains difficult. The multivariate receptor model delineates a source of high chromium content. But I have no knowledge of any distinct chromium source. This means that multivariate receptor models are appealing because only the receptor has to be monitored; but to use the results for discussing mitigation measures, the identification of the sources becomes essential.

Chapter 4 focuses on the soda ash industry effluent. The results show that the soda ash production increases the fine sediment load in the receiving water body so that roughly 30% of the fine sediment captured by the sediment traps originate from soda ash production effluent. In terms of clogging, this may be critical. In terms of sediment-associated inorganic pollutants, soda ash production is not critical. Indeed, particulate matter from urban wet weather discharge, which exhibits high element contents of high mobility, is diluted by particles from the soda ash industry. As a result the fine sediment downstream of the soda ash industry effluent is less toxic than upstream of the discharge point.

As stated above, the sediment traps do not resemble the bed sediment very well so that the intrusion of fine sediment is over-estimated. The question arises whether they resemble the suspended sediment load instead. With the results of chapter 3, it is possible to answer this question. The soda ash production site has a capacity of 430’000 t/a. About 3 kg particulate matter per produced t soda is emitted into the Bode River (Sodawerk Staßfurt 2008). This means that the soda ash production provides maximum 1’300 t/a particulate matter. As about 30% of the captured fine sediment originate from the soda ash production effluent, the total suspended sediment load should be about 4’300 t/a. The UFZ has measured the suspended sediment concentrations in Staßfurt biweekly. Between June 17, 2010, and June 8, 2011, the median suspended sediment concentration reached 14 mg/l. At a mean discharge of 13 m^3/s, the suspended sediment load reaches 5’700 t/a. This exceeds the above calculation by 30%. This indicates that the intrusion of fine sediment into the traps depends on the discharge dynamics. Soda ash production contributes disproportionally high to the captured fine sediment. This means that the intrusion of fine sediment mainly takes place during low flow.

This work has shown that multivariate receptor models allow to quantify the contribution of urban areas. It has further demonstrated that sediment traps are a valuable tool to capture the intrusion of fine sediment into the hyporheic zone. However, to define target values for particulate matter emissions from urban areas, more studies are needed. These studies should aim to delineate the relevance of the stressor "particulate matter" from other stressors such as altered discharge regime. The negative effects of particulate matter are due to clogging, organic matter content and sediment-associated pollutants. Interestingly, the surface water body act "Oberflächengewässerverordnung - OGewV" (2011), which came into force in Germany in July 2011, defines very high target values for inorganic priority pollutants. For the Bode River this means that the contents of zinc, copper etc. are uncritical. As a consequence, urban wet weather emissions of particulate matter are also uncritical regarding these priority pollutants. Considering that the Swiss directive for combined sewer overflow define target values of fine sediment emissions because of sediment-bound pollutants, it seems to be necessary to further delineate the effect of sediment-bound pollutants from sediment-associated organic matter, nutrients and clogging.

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