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Mapping the State of Sediment-bound Contamination in the Elbe Estuary

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Mapping the State of Sediment-bound Contamination in the Elbe Estuary

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Aim of the study within the project ImpleMenting MEasuRes for Sustainable Estuaries (IMMERSE)

The aim of the IMMERSE-activity *Mapping the state of sediment-bound contamination in the Elbe estuary* concerned in this work was to compile and assess existing field data from the Elbe estuary to summarize the state of priority particle-bound pollution in the estuary (and adjacent North Sea). This activity started in 2022 with the extension of the IMMERSE project by creating a cooperation with the research institute Helmholtz-Zentrum Hereon for sampling and chemical analyses in the Elbe estuary. Two PhD-studies started during the extension period of IMMERSE in both institutions (Hereon and BAW) with the purpose of improving the current understanding about the transport of selected heavy metals and persistent organic pollutants within the tidal influenced part of the Elbe river through a combined approach based on field studies, laboratory experiments and hydrodynamic numerical modelling including sediment transport in 3D (promoted within the BAW R&D-project CTM-Elbe, Contaminant Transport Modelling -Elbe).

The investigations advanced within IMMERSE and presented in this work, provide initial data for the development of a hydrodynamic transport model and deliver a first milestone for the umbrella project CTM-Elbe. The project CTM-Elbe will continue the investigations beyond the IMMERSE project lifetime to facilitate the ecological feasibility assessment of sediment relocation and explore solutions for sediment relocation that contribute to alleviate estuary pressures as tidal pumping and dredging cycles (sediment re-circulation) in the upper part of the Elbe estuary.

Introduction

For future permissions of sediment relocation strategies, for example with regard to the Marine Strategy Framework Directive (MSFD), it is expected that comprising environmental assessments about the spread of pollutants in estuaries are a prerequisite. To comply with the regulations of sediment management activities but also to better asses the chemical-ecological state of the estuary, it is important to further improve the existing forecasting tools, i.e. by means of numerical modelling, that could estimate the pathways and fate of contaminants in estuarine waters, sediments and suspended matter.

Estuaries have been identified as key environments in the global flux of trace metals (Fitzsimons et al. 2011). Some trace metals like Cadmium are highly poisonous, others like Zink can become toxic at larger amounts, therefore, the study and understanding of their fate as pollutants is of interest. The quantification of load fluxes and transfers of trace metals in different environmental compartments is still demanding, in estuaries particularly due to the temporal and spatial variability of estuarine processes. Water, sediment and suspended matter are key compartments that dynamically regulate metals transport and can uptake, carry and release trace metals in the aquatic environment. Besides metals, those compartments also transport organic pollutants, in fact, a huge number of new emerging pollutant classes have come up during the last decades such as pesticides, flame retardants or pharmaceuticals in natural waters.

To secure safe water depths in the navigation channel and port accesses at the Elbe estuary, sediments are dredged and relocated. Part of the fine sediments from upper estuary in the Hamburg area are contaminated due to legacy pollution that the river collects on its way across 1094 km from the source in the Giant mountains in the Czech Republic until the estuary. The heavy metals Cd, Cu and Zn belong to the priority pollutants that exhibit elevated concentrations in dredging material, therefore, their transport and distribution in the solid-water phases are of interest.

A data-based description of the current state of exposure in the estuary concerning the partitioning (e.g. transport in water, sediments and suspended matter) is still missing. This is necessary to develop a suitable numerical hydrodynamic transport model that estimates the drift and distribution of pollutants that are reactive to particle matter, i.e. those transported both, adsorbed by particles and dissolved in water. An appropriate preparation of measurement data for the development of the numerical hydrodynamic transport model for the Elbe estuary is an essential initial step. This work presents a first data evaluation of field measurements in estuarine conditions extracted from an extensive dataset of different sampling campaigns collected in the whole Elbe river, which embraced the simultaneous distribution of metals in the water-solid phases.

The partitioning of the heavy metals Cadmium (Cd), Copper (Cu) and Zinc (Zn) is here evaluated from the sampling data collected in between 1993 and 1998 and chemically analysed by the Helmholtz-Zentrum Hereon. In the Elbe, Cd and Cu and Zn are anthropogenic influenced elements (Aulinger et al. 2002), discharged and transported throughout the catchment, carried mainly by water, particles in suspension and sediments on the river bed. The spatial and temporary variation of metal concentration in the compartments water (in solution) and particle-bound (in suspended matter) is here analysed. The partitioning coefficient K_d, which is the ratio between particulate and dissolved concentrations, has been estimated to inspect possible influencing factors affecting the contaminant fluxes within the estuary.

The K_d coefficient has been largely studied in the works of Turner et al. (1992; 1993; 1996), among others, but to our knowledge, measurements of metal partitioning at the Elbe estuary have not been successfully implemented in a numerical hydrodynamic transport model that solves estuarine circulation and sediment transport. The evaluation in this report delivers initial data for the further development of a hydrodynamic transport model of this kind.

1. Materials and methods

1.1. Evaluation of existing data

Several sampling campaigns were undertaken between 1993 and 1998 in the Elbe river to examine the temporal trend and state of pollution (e.g. metals) and provide basis data for the development of a monitoring system in the River Elbe covering the whole river extension from the spring in the Czech Republic to the mouth at the North Sea in Germany. The water samples were acquired by helicopter sampling and analysed with four different multi-element methods (Aulinger et al. 2002). Data collection and chemical analysis was carried out by the GKSS Research Centre (now Helmholtz Zentrum-Hereon). The sampling methods, sample preparation and analytical analysis for the detection of elements has been published and evaluated by Prange (1997) and Aulinger et al. (2002). Aulinger et al. evaluated the data for anthropogenic charge. Using multivariate statistical methods, they characterized the metal variation in SPM and sediments between geogenic or anthropogenic influenced elements in the river Elbe.

In comparison to the aforementioned publications, this report focuses on the tidal influenced Elbe river from the weir at Geesthacht (40 km upstream from Hamburg, Germany) until the mouth at the North Sea. Physicochemical conditions in the estuary differ due to bidirectional tidal currents, mixing with saltwater and higher SPM loads from those upwards the tidal limit at freshwater conditions. The variability of those estuarine conditions is relevant for the characterization of key process governing the partitioning of the metals in water-solid phases, therefore, this work provides a data analysis of the metal distribution considering measurements within the estuary system. The sampling data are analysed for possible factors affecting the distribution of heavy metals in the water-solid phases. The variation of metal concentrations along the estuary are visualized and potential associations with water constituents by means of descriptive statistic evaluated. Correlations with SPM concentration and salinity are considered.

The sampling data analysed in this work considers the concentrations in water (dissolved) and SPM (particulate) of Cd, Cu and Zn, determined from the same water sample at a specific location along the estuary. Sediment was not sampled simultaneously (Prange 1997), thus, sediment measurements were not suitable to examine the metal distribution in comparable conditions, and not considered in this work. Particulate and dissolved concentrations were employed here to calculate the partitioning of the heavy metals under estuarine conditions.

The number of samples for Cd, Cu and Zn with the corresponding campaign dates are depicted in table 1. Cu and Zn were sampled in autumn and spring from 1993 to 1996 during the same campaigns. The data for Cd dated from 1996 to 1998. Besides the concentrations of Cd, Cu and Zn in dissolved and particulate form, also the SPM concentration was available for the majority of the samples but not for all. Thus, the association of metal concentrations with SPM presented in section 2.3 depicts a selection of data included in Table 1.

Table 1. Date and number of samples taken in the Elbe estuary during 1993 to 1996 considered in this work (data provided by Hereon).

CADMIUM		**COPPER**		**ZINC**	
Date survey	**No samples**	**Date survey**	**No samples**	**Date survey**	**No samples**
10.09.1995	20	04.10.1993	24	04.10.1993	25
21.04.1996	11	09.05.1994	34	09.05.1994	38
06.09.1998	10	10.09.1995	36	10.09.1995	36
07.12.1998	10	21.04.1996	36	21.04.1996	37

Figure 1 depicts the distribution of the samples in the Elbe estuary. The tidal limit is located next to the Elbe km 590 at the weir Geesthacht, and the mouth of the river into the North Sea by Cuxhaven, Elbe km 730. The farthest samples in the German Bight were taken at the Elbe km 750.

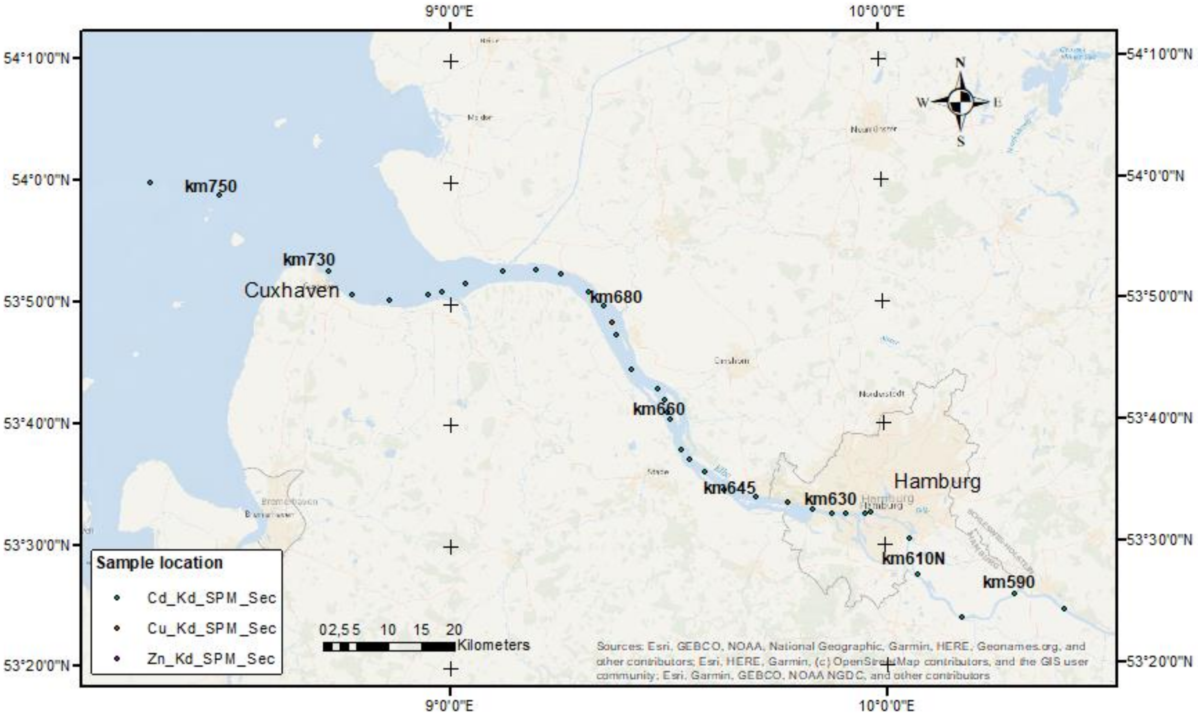

Figure 1. Samples location in the Elbe estuary. Elbe-km from 590 Elbe-km (Geesthacht) to Elbe-km 750 in the German Bight (data source: Hereon)

1.2. Partitioning in water-solid phases

The distribution of heavy metals in the phases solid-water can be parametrised by means of partition coefficient K_d, which gives the ratio between the concentrations in particulate and dissolved form found in the water column (see eqn [1]). In the sampling campaigns aforementioned, the metal concentration bound to the suspended matter in particles smaller than 20 µm was determined, as well as the dissolved concentration found in the water samples (0,45 µm filtrate), and with these two concentrations the K_d coefficient was calculated for every sample location.

[1]. Partition coefficient

$$K_d = \frac{[P]}{[D]} \ \frac{(mg\ kg^{-1})}{(mg\ l^{-1})}$$

The concept of the partitioning coefficient K_d as an empirical parameter is widely used for modelling trace metals fate in natural waters. However, measured K_d-values can be difficultly transferred from one location to another (Balls 1989) since the geochemistry and hydrodynamic forces in different estuaries are rather heterogenous.

The development of an appropriated partitioning approach in the Elbe estuary based on a hydrodynamic transport model requires estimates about the K_d parameter and an understanding about the relative importance of variable environmental conditions for the transport of pollutants. As shown in Figure 2, different complexity levels can be defined modelling contaminants in water bodies. Depending on the model application and scale of interest, a different degree of detail and complexity is required.

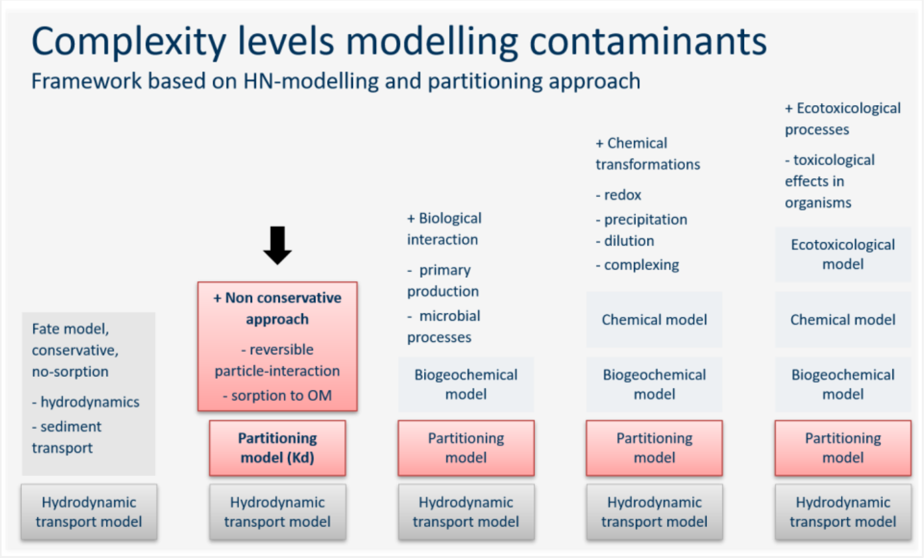

Figure 2. Complexity levels modelling contaminants within a framework based on HN-modelling and a partitioning approach

The degree of detail concerned here deals with the pollutant behavior at estuarine scale, assuming parametrization or neglection of fine-scaling processes (in time and space) that play a subordinate role in the distribution of pollutants across the estuary. That encompasses a modelling approach that solves the hydrodynamics and sediment transport in the estuary and parametrize the partitioning by means of K_d as represented in red at Figure 2.

2. Results - Evaluation of existing data

2.1. Distribution of Cd, Cu and Zn in the estuary from 1993 to 1995

Under estuarine conditions, the K_d parameter is expected to vary, since the partitioning (i.e. the phase change of a metal from dissolved to the particle-bound phase) is influenced by changes on physicochemical conditions in the estuary like SPM concentration, salinity, temperature, pH or dissolved oxygen saturation. Particularly, salinity and SPM concentrations depict in general sharp spatial gradients along the estuary that can alter the equilibrium of pollutants in the water-solid phases.

The resulting K_d values in each field campaign along the estuary are depicted in Figure 3 (Cd), in Figure 4 (Cu) and Figure 5 (Zn). The partitioning of Cd varies along the river. A decrease towards the North Sea is evident particularly in the sampling data of September 1995; the K_d decreases one order of magnitude from mid-estuary to the mouth. The sampling campaigns in 1996, 1998 show the same pattern. The samples from upper estuary in September 1998 confirm the spatial tendency of larger K_d-values in the estuary section dominated by the fluvial influence. The time variation of the K_d cannot be well distinguished from the data because the sections sampled in autumn were different to those sampled in spring.

Zinc and Copper were determined in the same four sampling campaigns during fall and spring from 1993-1996. Both elements delineated seasonally and spatially variations. A decreasing partitioning from the tidal limit from Hamburg towards the mouth is also observable for Zn and Cu. The reduction of K_d towards the sea reached one order of magnitude for Zn. For Cu the reduction was less pronounced.

In the turbidity maximum zone (TMZ), a seasonal influence can be inferred; the K_d for Cu next to the TMZ depicted higher values in spring 1994 (right, top in Figure 4) than in fall 1995 (left, bottom in Figure 4). Zn depicted lower K_d-values in spring 1994 and 1996 (right, top and bottom in Figure 5), than in fall 1995 (left, bottom in Figure 5). The apparent seasonality seems to be weaker than the spatially variation observed along the tidal river, however, these observable variation between spring and fall in the four sampling campaigns is a result of overlapping non-linear estuarine dynamics.

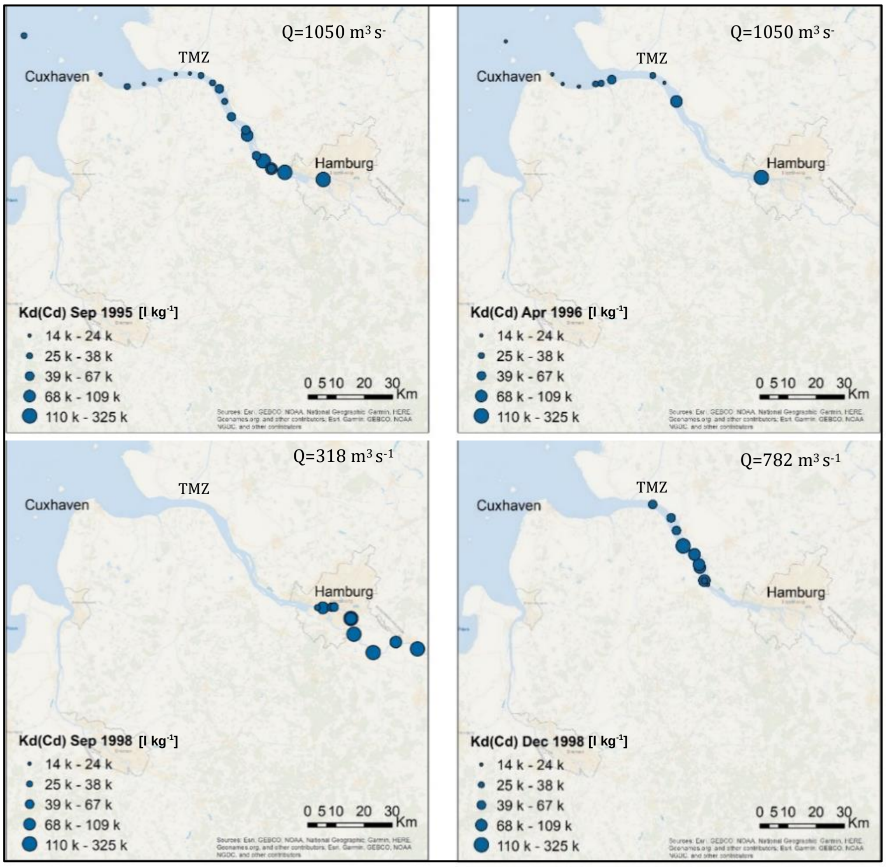

Figure 3. Partition coefficient K_d along the tidal river Elbe for Cd in the surveys from 1995 to 1998

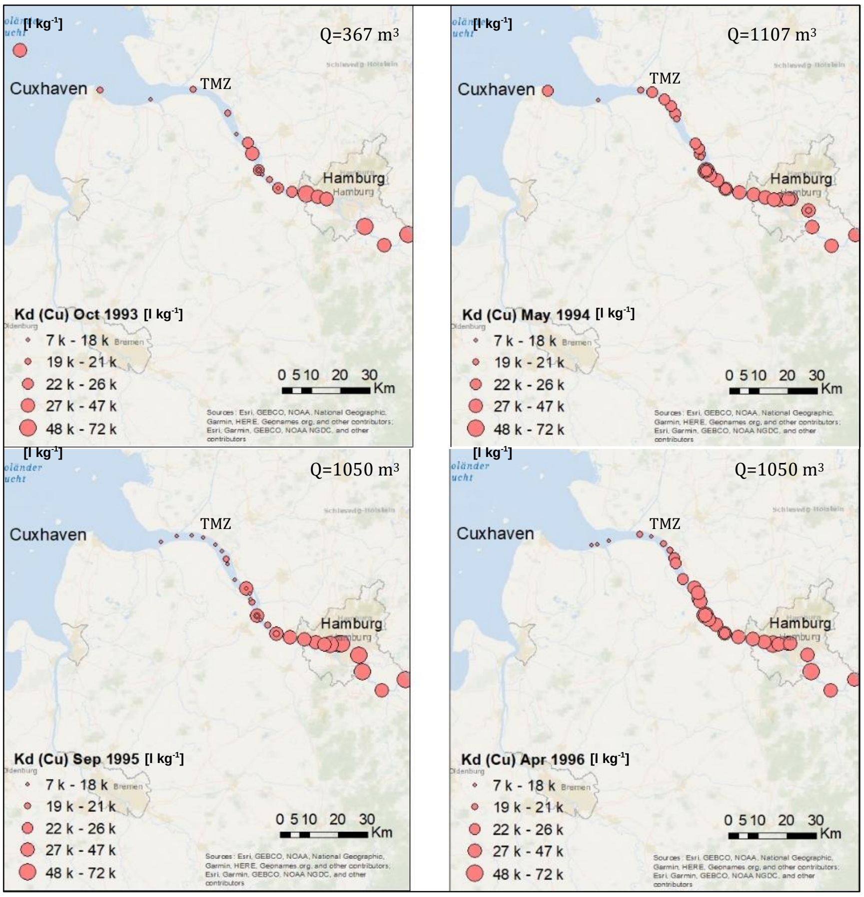

Figure 4: Partition coefficient K_d along the tidal river Elbe for Copper in surveys from 1993 to 1996

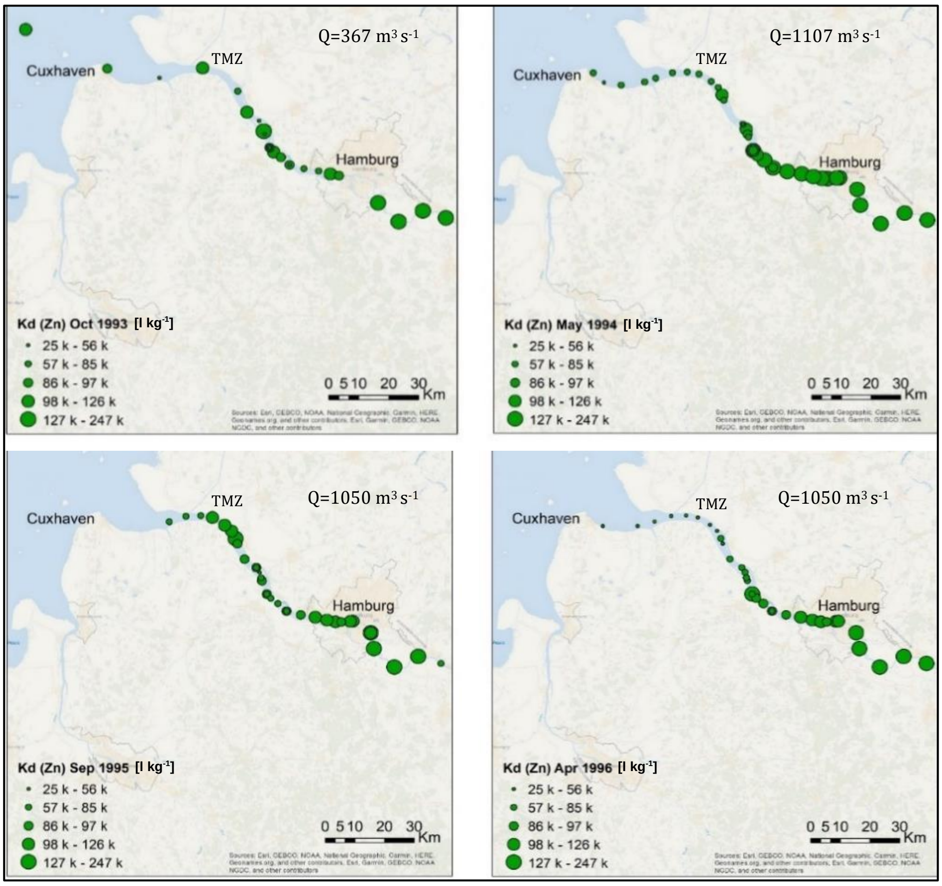

Figure 5. Partition coefficient K_d along the tidal river Elbe for Zinc in surveys from 1993 to 1996

2.2. Variation of the K_d parameter over different seasons

The variation of K_d over the estuary per sampling campaign and element is depicted by box charts in Figure 6. Each box depicts the 25th and 75th percentiles and the median (edges of the box, and middle line, respectively) of the K_d-values for the samplings in spring and fall, respectively. The notches (blue band areas) show the confidence interval of the median at 95 %. The notches of the four box charts per heavy metal overlap, meaning that the median K_d in each sampling campaign did not differ at the 5% significance level.

Zinc depicted the highest K_d values and also the most evident seasonal variation of the three metals. In Spring May 1994, the 25th and 75th percentiles were 0.7×10^5 and 2×10^5 for Zinc, whereas the distribution for Copper and Cadmium varied the most in autumn, Sep-1995 with 25th and 75th percentiles equal to 1.55×10^4 and 4.4×10^4 (Cu) and 0.6×10^5 and 1.5×10^5 (Cd), respectively. Compared to Zinc and Cadmium, Copper shows the lowest K_d-values in all sampling campaigns.

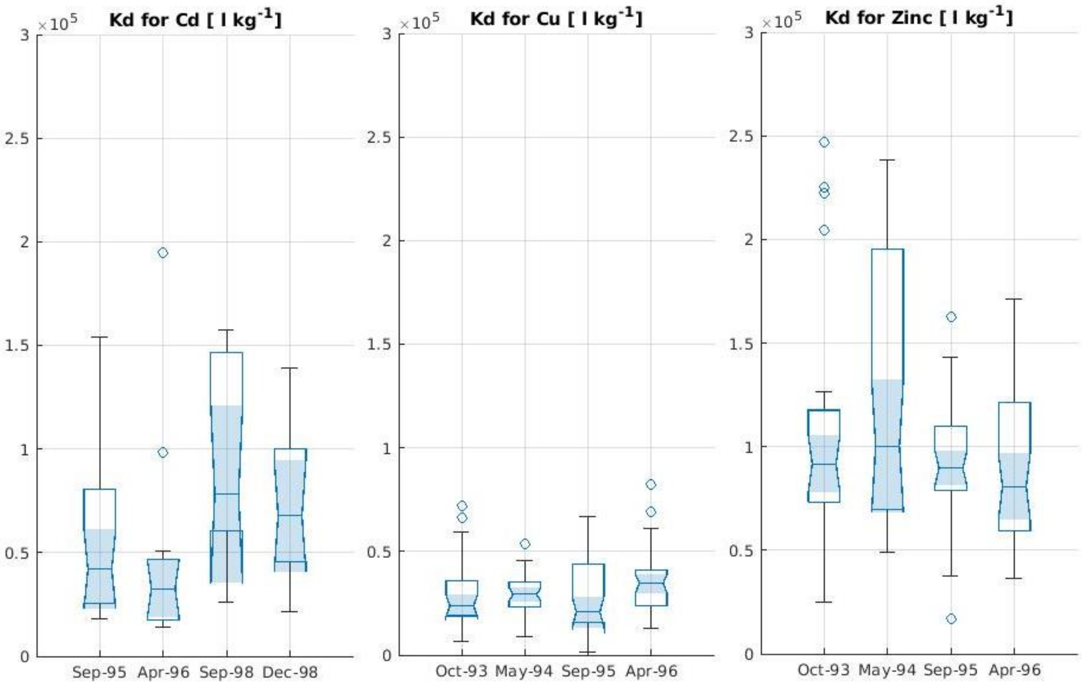

Figure 6. Variation of the partition coefficient for existing data (1993-1998). Data provided by Hereon

2.3. Influence of suspended particulate matter

The K_d parameter indicates the ratio between particulate and dissolved concentration, thus, its variation depends on the metal concentration in each phase, and those concentrations might be coupled with each other but not necessarily. To which grade the metal concentrations in water and particle-bound correlate with each other depends on natural and anthropogenic factors. SPM concentration and its composition is expected to alter the particle-bound concentration of pollutants like heavy metals and in case of partitioning, variations on both water-solid phases are expected for example when truly dissolved and not complexed metals are rapidly adsorbed on the surfaces of fine particles (Morris 1990).

In Figure 7, the particulate and dissolved concentrations of Cd, Cu and Zn over SPM concentration is depicted. The behaviour of the metals in the particulate phase with SPM concentration appears to be non-linear inversely associated. SPM concentrations greater than 100 mg l^{-1} seem to reach a threshold from which on the particulate concentration is low and invariable with increasing SPM concentration. This representation gives insights on the upwelling and mixing of unpolluted marine sediments that become predominant to fluvial sediments in increasing SPM concentrations towards the mouth of the estuary. Metals are indeed associated to the small particle sizes and matter content that principally dominate the low SPM concentrations in the upper estuary. In general, high bulk SPM concentrations are mediated by strong tidal shear stresses, which can both, bring coarser particle sizes from the riverbed in suspension, but also disrupt fragile flocs into very small particle sizes that are rather measured in the 'operative' dissolved concentration (filtrate < 0.45 μm) than the SPM-bound concentration. The combined effect of dynamic mixing and sorting of particles in suspension along the estuary seems to primarily contribute to the decrease of metal concentration with increasing SPM.

The dissolved concentration of Copper appears to be substantially unrelated to the SPM, the correlation coefficient was in all field campaigns less than 0.2 (see Table 2). The dissolved concentration of Cadmium and Zinc outlined some weak, mainly inverse association with SPM.
In the field campaigns in 1998, only Cadmium samples were available and in different sections of the estuary (Figure 5). That means that the relative high correlations of the particle concentration (r =0.67 in Sep-98) and dissolved fraction (r = -0.64 in Dec-98) with SPM concentrations are not representative for the whole estuary, they rather give insights of the relative importance of predominant processes in these sections. For instances, particulate and dissolved Cd collected in Sep-98 at the fluvial zone of the estuary (under low SPM concentrations < 50 mg l^{-1}) depicted positive, relative high correlations with SPM (r = 0.67 and r = 0.45, respectively). This contrasts particularly with the negative (weaker) correlation evidenced in the rest of the particulate data for SPM concentrations greater than 100 mg l^{-1}.

Despite that, the influence of the turbidity maximum zone in mid-estuary on the Cd concentration can be inferred from the data of Dec-98. Those samples coincide with the estuarine transition zone, where the SPM continuously increase towards the sea and the influence of marine loads become predominant (brackish waters). Here, both, particulate and dissolved Cd depict an inverse correlation with SPM (r= -0.37 and r = -0.64 respectively), which give insights on the dominant influence of mixing in the estuary transition zone on the Cd concentration, involving the operative dissolved Cd with a relative high correlation coefficient.

Table 2. Correlation coefficient between heavy metals (particulate and dissolved concentration) and SPM concentration

r (Cd, SPM)			***r (Cu, SPM)***			***r (Zn, SPM)***		
Date	Par.	Dis.	*Date*	Par.	Dis.	*Date*	Par.	Dis.
Sep-95	-0.34	-0.16	*Oct-93*	-0.22	0.10	*Oct-93*	-0.41	-0.19
Apr-96	-0.03	0.35	*May-94*	**-0.61**	-0.17	*May-94*	**-0.53**	0.36
Sep-98	**0.67**	0.45	*Sep-95*	-0.45	0.09	*Sep-95*	-0.43	-0.33
Dec-98	-0.37	**-0.64**	*Apr-96*	-0.42	-0.06	*Apr-96*	-0.43	-0.37

The concentration of particulate Zinc behaves similar than Copper; an inverse association can be noticed, where from 100 mg l^{-1} up, the particulate concentration rapidly decreases. However, the dissolved Zn does differ from dissolved Cu; Zn depicts a weak inverse association with SPM concentration. In Spring, dissolved Zn over SPM concentrations greater than 100 mg l^{-1} were in general higher than in autumn.

The apparent association of the solid and water phases of metals with SPM concentration cannot lead alone to a conclusion about the functional relationship of these metals with SPM in the estuary. Other relevant factors in the water-solid distributions were acting simultaneously with increase of SPM concentrations, like SPM composition (grain-size and organic content), salinity gradient and the retention times that also increase with distance from the tidal limit to the mouth. Nevertheless, an inverse association of the particulate metal concentration with the SPM concentration is evident, and the absence of an association of dissolved Cu with SPM is noteworthy.

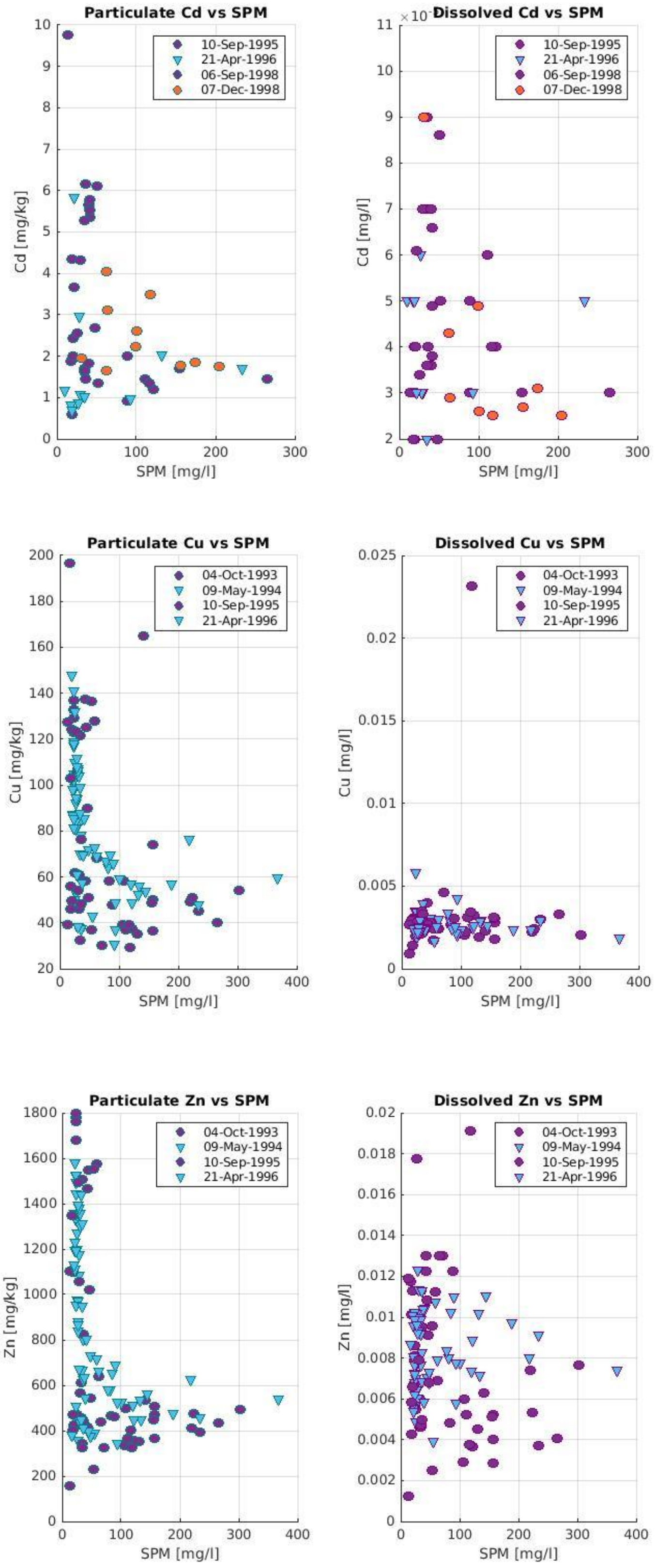

Figure 7. Dependency of the particle and dissolve concentrations of Cd (top), Cu (middle) and Zn (bellow) with the SPM concentration on [mg l^{-1}]

2.4. Variation of K_d coefficient in characteristic physical conditions

Besides the SPM concentration, the distribution of heavy metals is expected to be influenced by the salinity gradient as ions in seawater compete for active sites on the surface of the particles and adsorbed metals can form stable complexes and go into solution. Both situations can lead to a removal of particle-bound heavy metals at the salt front, and in turn, to an increase of the dissolved concentration with the consequence that the K_d coefficient decreases.

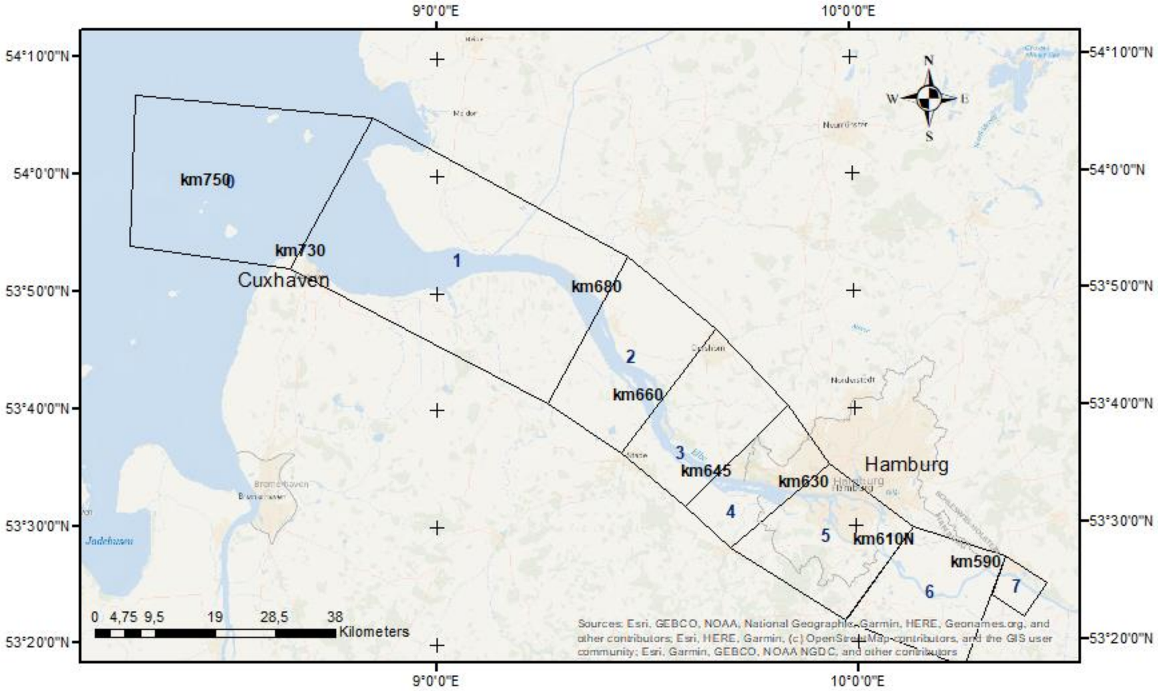

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Figure 8. Location of sections characteristic for physical conditions in salinity and SPM relevant for the variation of the K_D coefficient in the estuary

To analyse the behaviour of the three metals with respect to the salinity gradient in the Elbe estuary, the variation of K_d coefficient is considered within different sections along the estuary (with exception of section seven), where characteristic physical conditions regarding salinity but also SPM concentration and composition are expected to be less heterogenous, or at least less pronounced than when regarding the variation along the whole estuary (see Figure 8).

Section seven is not tidal influenced and can be seen as a reference for the absence of estuarine mixing and tidal influence. The environment conditions in summer upstream the tidal limit at section seven differ the most to the estuarine conditions (e.g. dissolved oxygen saturation, pH, organic composition and temperature). Moreover, this section is not affected by dredging and relocation of sediment, which instead is necessary downwards from Hamburg in the Elbe estuary. Section six is tidal influenced but fluvial predominated. The retention times are typically between hours and days, one order of magnitude shorter than at the mouth of the estuary. In section six, the organic content and dissolved oxygen are in general much higher than elsewhere in the estuary. Section five encloses the main area of the Hamburg harbour with deep channels, high sedimentation rates and lower oxygen saturation and recurring dredging works. From section seven to section five, the organic content is higher than downwards, in section five the tidal range reaches its peak along the tidal Elbe river.

The K_d variability within each of the sections is presented through box diagrams in Figure 9.
The variation of the K_d within the eight sections from upwards the estuary (section 7) towards the mouth of the estuary (section 0) is depicted in Figure 9. In the upper estuary, within the sections five to seven, the K_d values are in general greater. A general reduction of the K_d coefficient is observed for the three metals. Particularly, the variability of the K_d for zinc decreases with distance from the tidal limit; high temporal variation remains in the upper estuary (sections 5 to 7). This could be accounted for the seasonal variability observed in spring and autumn in the estuary (Figure 6), which is expected to be higher in the upper estuary, due to the rapid changes in organic content and absence of dilution with seawater. Cd depicted in section four an unexpected increase; in this section only two samples were taken, and in two different seasons (Sep-95 and April 96), therefore, this might be not representative to indicate an anomality in the decreasing trend towards the mouth.

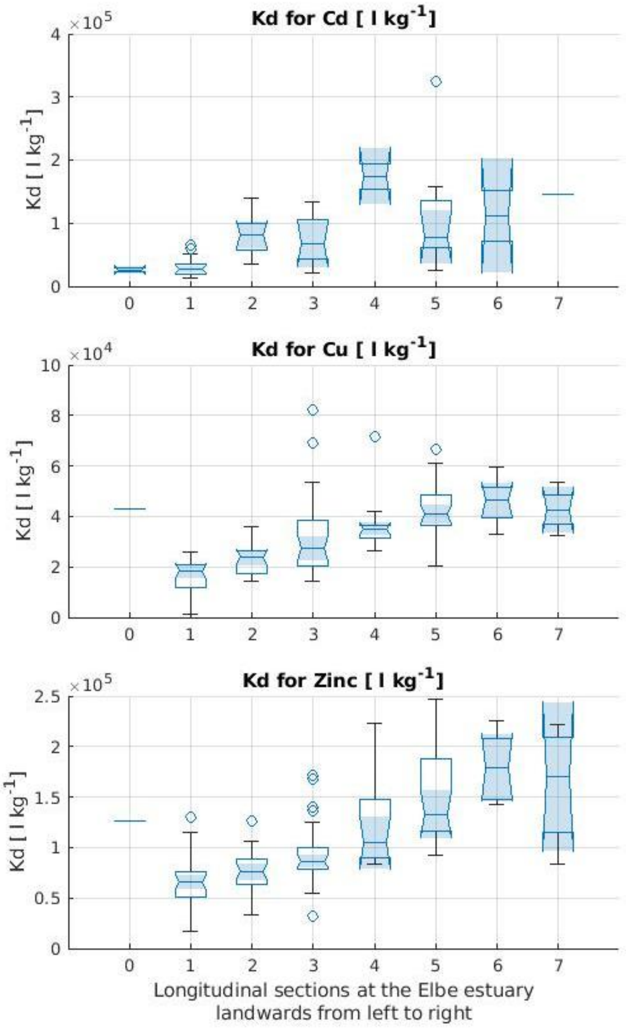

Figure 9. Variation of the K_D coefficient within eight selected sections along the estuary. Right towards tidal limit (section 7), left towards North Sea (section 0). Notice that the scale of K_D-values is different in each diagram.

Comparing the seasonal with the spatial variation, it appears that the factors influencing the spatial variation of the K_d along the estuary are more significant than the factors causing seasonal differences in the partitioning. That holds in particular for the lower estuary, where the difference between the 25th and 75th percentiles in the three metals becomes closer.

Two factors might be related with the observed variation of the K_d in the estuary: the influence of seawater and marine sediments diluting the pollutant loads towards the mouth of the estuary, and the shorter retention time in the upper estuary, where seasonal changes by high and low freshwater discharges and inputs of 'fresh' organic matter invoke sorption reactions that do not last long enough to achieve equilibrium. Chemical and biological reactions might be neglectable or not evident in the lower estuary due to large water masses and SPM concentrations towards the turbidity maximum zone (TMZ), whereas the dynamics of the upper estuary with relatively small tidal volume and large tidal range are more likely to evidence ongoing sorption processes, noticeable in the variability of measured concentrations. The impact of dredging and relocation of sediment by injecting (at least) temporary particles in suspension was not exanimated in the data collection, but this influence is implicit in the SPM measurements. In particular, for the sampling campaigns in 1998, the SPM was influenced by the deepening works of the navigation channel in the Elbe estuary that started in December 1997.

3. Discussion

The partition coefficient K_d for Cd, Cu und Zn in the Elbe estuary presented in this work were in the same order of magnitude than the K_d values found at other North Sea locations for instances in the estuaries Weser (Germany), Scheldt (Belgium) and Humber (Great Britain) reported by Turner et al. (1992; 1996).

The observed decrease on the concentrations and K_d coefficients for the heavy metals Cd, Cu and Zn towards the North Sea has been largely observed in several estuaries of the North Sea since 1990 (Turner et al. 1992; Fitzsimons et al. 2011). This inverse correlation with distance towards the mouth is well known, however, the driving mechanisms are found ambiguous in the literature. Physical mixing of fluvial sediment with marine sediment is a major driver in decreasing the particulate concentration towards the mouth, but this alone does not explain the variation of the K_d along the estuary. Different physicochemical processes are simultaneously interacting and their relative importance for changes on K_d depends on the estuarine environment. For example, specific conditions related to the biogeochemistry and hydrodynamics of the estuary (i.e. location of the salt front, turbidity maximum and retention time) but also anthropogenic factors like dredging and relocation of sediment to maintain the fairway. Besides estuary-specific conditions, also variable measurement and analytical procedures have made the interpretation of metal behaviour in different estuaries and the discrimination of the influencing factors challenging.

The association of trace metals with colloids has been argued to be a reason for the inverse association of K_d with SPM (Fitzsimons et al. 2011) suggesting that the operational dissolved concentration (pore size = 0.45µm) includes metals adsorbed by colloids, which increase with SPM concentrations.

Following that, colloids will influence the metal concentration measured in the operational dissolved concentration in association to the SPM behaviour. This effect could be inferred from the data collection evaluated in this report for Zn and Cd but it was not observed for Cu, at least it was not detectable in the observations (within the scale and analytical methods employed). The measured Cu in solution, which included potentially adsorbed Cu by colloids, did not depict an association with increasing SPM. The variation of K_d for Cu was mainly driven by changes on the particulate Cu but not accompanied by an increase in dissolved Cu. On the contrary dissolved Zn and Cd depicted a weak association with SPM, similar to the relationship of the particulate concentrations with SPM. The inverse correlation with the SPM seems to be primarily influenced by the import of marine suspended material into the estuary (coarser material) as well as the upwelling of particles and porewater depleted of metals. The change in concentration (and composition) of SPM is expected to cause a shift in the relative proportions of the metal in solution and particle bound (Turner et al. 1993).

Despite that, the observed variation of K_d with particle mixing along the estuary might be related with low and high freshwater discharges, but this effect cannot be segregated from the SPM or salinity effects in the sampling data. Aulinger et al. (2002) suggested that high particulate concentrations in May 1994 were a result of the unusually high discharge in April 1994. He concluded that higher particulate concentrations of metals in spring with respect to autumn were a result of the much solid material carried into the river waters in spring compared to the dominant seaward transport in autumn. Following that, the retention of material discharged during April 1994, i.e. still trapped in the estuary and therefore measured in May 1994, would have led to high particulate concentrations.

The seasonal effect observed in this study was evident for the dissolved concentration of Zn. The concentrations of dissolved Zn were higher in spring than in autumn for similar SPM concentrations up to 50 mg l^{-1} (bottom of Figure 7, right). This interplay between particulate and dissolved Zn in spring seems to be relevant for the variation of the K_d coefficient, which depicted the largest interquartile range between the 25th and 75th percentiles in May 1994. The key processes responsible for that could not be deduced from the dataset since the river flow conditions acted simultaneously on the location of TMZ, brackish waters and retention times of particles in the estuary. Also, a seasonal effect could be related with the chemical reactions induced by changes on SPM composition (organic ligands), pH and temperature.

From the observed variation of the metals with respect to SPM (Figure 7, left), a relationship with the smaller grain size fractions can be inferred, in which the organic matter content might be relevant. According to Mosley and Liss (2020), Cu is found in estuaries in most of the cases (>99%) strongly bound to an unidentified organic ligand present a low concentration in the water column. The relationship of particulate Cu with SPM observed in this work agreed with that findings. Particulate Cu reflected high concentrations on a fraction of the SPM, only present in the small SPM concentrations. For SPM concentrations higher than 100 mg l^{-1} the metal concentration remained low and invariable. Particulate Zn and Cd depicted a similar pattern. This behaviour can be compared with the grain size sorting that occurs when the enhanced tidal shear stress induces large SPM concentration and disruption of flocs. That results in small particle sizes at high bulk SPM concentrations. Fitzsimons et al. (2011) depicted this relationship from field measurements in the Tamar estuary; for SPM concentrations below a threshold, in that case 200 mg l^{-1}, the median particle size evidenced large variation, but for SPM concentrations greater than approx. 200 mg l^{-1}, the median grain size remained invariable below 100 µm. Similarly, particulate Cd, Cu and Zn but also dissolved Zn and - to a less degree dissolved Cd did not vary with SPM concentration larger than 100 mg l^{-1}. In fact, particulate Cadmium correlated positively with SPM concentration smaller than 50 mg l $^{-1}$ (r=0.67). That evidenced the strong dependency on the content of SPM related to the smaller particle sizes and the importance of resuspension and transport of SPM in modelling the partitioning of these metals.

Besides the metal sorption, it is established that complexation is a relevant influencing factor affecting the speciation of heavy metals with salinity, in particular influencing the partitioning of Cd. The seawards decrease of the K_d coefficient for Cd has been attributed to the formation of high stable and soluble chlorocomplexes (Turner et al. 1993). These findings agreed with the observations of this report. The K_d decrease for Cd was at most pronounced over the salinity gradient.

Turner et al. 1993 distinguished between a fraction in the particulate concentration that is leachable (through analytical procedures) and therefore available for exchange, from a particulate fraction strongly bound to particles and less prone to undergo desorption. This was not analysed in the available data. The application of the calculated K_d-values for modelling are meaningful for the setup of initial conditions and for validation purposes of particulate and dissolved concentrations but more knowledge about the relative importance of the transferability of particle-bound pollutants in the Elbe estuary is necessary for the understanding of the factual metal partitioning in water and SPM.

4. Conclusions and outlook

The overall objective of the IMMERSE project that supported this study was to contribute identifying sustainable sediment management strategies, for instances, by forecasting the drift and potential accumulation of pollutants in different places within the estuary or their transport into the North Sea. The purpose of this study was to deliver a first milestone in the development of a numerical hydrodynamic transport model for the Elbe estuary that aims to characterize relevant processes in the partitioning of particle-bound pollutants, in such a way that the transport behavior of priority pollutants is optimally reproduced by 3D-hydrodynamic modelling. An extensive sampling dataset along the estuary was examined here, which provided first insights about influencing processes in metal partitioning, as well as initial input for the setup and validation of the modelling approach coupling transport and partitioning of the heavy metals Cd, Cu and Zn.

Existing data from field campaigns during 1993-1998 for the heavy metals Cd, Cu and Zn in the Elbe estuary have been re analysed with respect to the variation of the partition coefficient K_d.
Comparable results were found to former measurements in different estuaries of the North Sea Region. Remarkable was the relative importance of Zn and Cu to the fraction of SPM below 100 mg l^{-1} and the high spatially variation of the K_d towards the North Sea (one order of magnitude for Cd and Zn). However, the driving mechanisms causing the variations of the metal concentrations in the Elbe

estuary could be inferred but not explained by means of the sampling data analysed in this work; key factors affecting the distribution in dissolved and particulate form like SPM (concentration and composition), salinity gradient and retention times are associated on each other and acting simultaneously on the metal speciation along the estuary. Furthermore, the measurements of dissolved and particulate concentrations might reflect a history of resuspension and deposition as well as several short and long-term sorption and desorption reactions along the river. A separation of the processes acting simultaneously in the estuary is not possible by means of in-situ measurements. Hereby numerical models are meaningful scientific tools to investigate the separated effect on partitioning of, for instances, natural physical mixing and resuspension of sediments at estuary-scales, despite changes on SPM composition or other anthropogenic influences like dredging and relocation of sediment as well as unknown pollutant sources.

In fact, both laboratory and numerical experiments are further necessary to simulate the mechanisms driving the partitioning of the pollutants separately, and derive the relative importance of the related process such as the hydrodynamic and sediment transport, sorption and complexation processes. The field data analysed here gave a general understanding of estuarine factors acting on the partitioning, however, the apparent associations must be in detail investigated with help of numerical modelling experiments to account for the hydrodynamics and key factors at estuary-scale, and laboratory experiments to study the speciation of the pollutants under controlled variation of physico-chemical conditions.

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