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About the Transport and Distribution of Organic and Inorganic Sediment-bound Pollutants in Estuaries and Coastal Waters

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Content

Introduction

Heavy metals and persistent organic compounds are common legacy pollutants transported by riverine and air currents into estuaries of the North Sea region. In the water column, they drift either dissolved with the stream velocities, or particle-bound with the velocities of suspended particulate matter and sediment travelling on the river bed. Using water or particles as a transport medium, pollutants travel through and in between different environmental compartments including air, biota, estuarine waters, suspended material and bed sediments. Due to particle settling and sedimentation, particle-bound pollutants are prone to end up and accumulate in the bed of rivers and seas. In this manner, pollutants at trace levels are continuously released into estuarine and seabed sediments, from regional to global scale (Chiaia-Hernández et al. 2022).

This report provides a concise review about relevant processes in dynamic estuaries like the Elbe estuary, which influence the transport and as a result the distribution of pollutants at estuarine scale. Concepts and approaches relevant for modelling the transport of particle-bound reactive pollutants are discussed. The inorganic and organic substances dealt with in this work play a role in the sediment and estuary management at the Elbe estuary since they are present in legacy wastes from the whole Elbe catchment, for instances from mining, industrial, agriculture and domestic activities (Heise et al. 2007), and are continuously transported from upstream into the estuary and adjacent coastal waters.

Hereafter, “pollutant” refers in general to the heavy metals Cd, Zn, Cu, Pb and the organic compounds: hexachlorobenzene (HCB), polychlorinated biphenyls (PCBs), dichlorodiphenyltrichloroethane (DDT) and its metabolites. Those are the most common legacy pollutants in North Sea estuaries aside a huge number of new emerging pollutant classes which came up during the last decades such as pesticides, flame retardants or pharmaceuticals.

Particle-reactive pollutants can spread in estuarine conditions through water, suspended particulate matter (SPM) and through resuspended sediments transported near to the riverbed (Figure 1). The tendency of a pollutant to be transported in the water-phase, dissolved, and in the particle-phase, particle-bound, is determined by the chemistry of the pollutant (in general by hydrophobicity and polarity), the particle properties, and by the physicochemical conditions of the estuary like for instances pH, temperature, salinity and the organic and inorganic matter available.

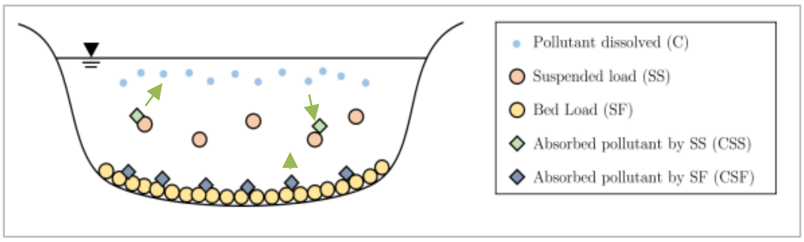


Figure 1. Simplified adsorption and desorption of pollutants in SPM and sediments

A redistribution (i.e. partitioning) of the pollutant concentration in the water-solid phases occur in general by adsorption and desorption at the surface of particles. Under steady state conditions and attainment of chemical equilibrium, a stable concentration in both-phases would set. However, under dynamic estuarine conditions, chemical equilibrium is likely not achieved (Morris 1990). In estuaries, the gradients in salinity, SPM and organic matter content are typically pronounced and that influence the thermodynamic drive for sorptive exchanges. Also, large water residence times and tidal shear stresses affect the interactions between dissolved chemical species and particle-surfaces in the water column.
In the following, physical and chemical aspects under estuarine conditions affecting the partitioning of pollutants in estuaries are discussed.

1 Influence of natural physical mixing in pollutants distribution

Physical mixing is a major drive for the distribution of pollutants in estuaries and pollutant loads flowing out to the seas. The convergence of freshwater with seawater fluxes in the estuary induces advective and diffusive mixing, and particles in the water column may undergo several internal cycles before they are exported to the sea. Especially, dynamic estuaries encounter naturally strong mixing through estuarine circulation and turbulence, which has an effect on the uptake and removal of dissolved pollutants from the water column, and on the kinetics of the chemical reactions.

1.1 Dilution effect

One major consequence of physical mixing in estuaries is the dilution of polluted loads from fluvial sources when fluvial loads mix and disperse seawards by means of advective and diffusive transport. In general, streams loaded with pollutants end up in the estuary and mix gradually with greater masses of seawater and marine particles, which are depleted of pollutants. In this manner, marine particle-water fluxes dilute fluvial pollutants and both, pollutant in solution and particle-bound, are gradually reduced from up estuary to the mouth. The typical dilution patterns depict high pollutant concentrations in sediments next to historical contamination sources and decreasing concentrations downward close to the river mouth. This has been observed in the last decades for heavy metals in the Elbe river, where fluvial streams from tributaries and inland waters release legacy pollution that diminished in the tidal influenced Elbe river; particularly, the concentration of particle-bound pollutants is gradually reduced with displacement towards the North Sea (Heise et al. 2007; Heise et al. 2008).
Despite the reduction in particle-bound concentration, the dilution effect exerted by advection, does not reduce the net load of transported pollutants. The tidal excurse and net retention time of particles within the estuary might delay the export of the input loads out of the estuary, but the apparent reduction of loads through dilution, is rather a redistribution of the contaminant concentration that might shelter the risk of bioaccumulation of weak degradable pollutants.

Assuming that the concentration of a non-reactive pollutant in both water and solid phases from a fluvial source is affected only by the dilution effect on its way to the sea (without sorptive exchanges and neglecting other sources or sinks), the distribution of the dissolved pollutant is solely controlled by the hydrodynamics of the estuary. A conservative concentration in both phases is implicit and the dissolved concentration will be transported by advection and diffusion absent of uptake or releases due to particle interactions.

By means of the linear mixing curve (Figure 2), the conservative (or non-conservative) behavior of metals has been studied in estuaries, i.e. by interpolating the dissolved metal concentration between samples at the head estuary (freshwater endmember) and at the mouth (seawater endmember) over salinity as a conservative tracer towards the mouth (Boyle et al. 1974).

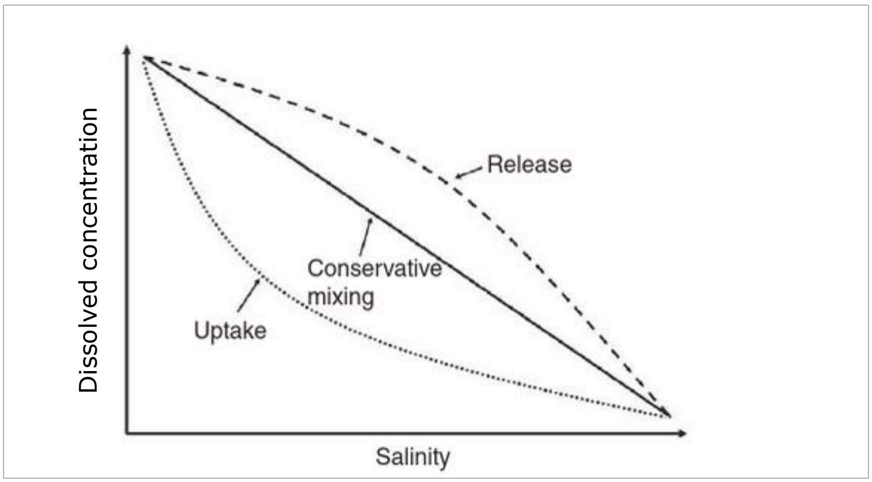


Figure 2. Schematic linear mixing curve. Taken from R.W.P.M. Laane et al. (2011) (modified).

A conservative mixing will depict a linear decrease in pollutant concentration as a result of mixed and diluted fluvial loads with seawater over salinity (Figure 2). However, the conservative mixing of some metals investigated in this manner at different estuaries resulted ambiguous as showed by Mosley and Liss 2020 (Figure 3). For instance the heavy metals Cu, and Zn were found both, conservative and non-conservative. Mosley and Liss 2020 argued that the characterization of the conservative behavior of a pollutant as that from a relation between two endmembers from freshwater and the mouth is problematic. Different pollutant sources might exist in between the two endmembers, like for example fluxes from tributaries or unknown discharges, which cause a nonlinearity in the mixing curve and which are interpreted as the non-conservative behavior of a reacting pollutant. Besides that, the intra-estuary comparison of the collected data is challenging due to diverse analytical methods and sampling procedures applied in different tide-dependent conditions.

Against this backdrop, the conservative or non-conservative transport of dissolved metal concentrations can be hardly explained alone by the dilution behavior observed in measurements at a certain environment condition sampled at a fixed time and place, suppressing for example unknown sources and sinks. Thus, a comprising sampling dataset accounting for potential sources and variable estuarine conditions is an important precondition for further analysis and use of modelling techniques.

Table 1. Estuarine mixing behaviour of metals (Fe, Pb, Zn, Cu) in selected studies globally

Conservative *v.* non-conservative patterns reported is for the ~<0.4-µm filtered fraction, although truly dissolved metals may behave differently to this fraction as noted in the text

Metal	Estuarine behaviour	Reference and estuary studied
Fe	Non-conservative mixing (removal)	Boyle *et al.* (1974), Merrimack, USA
		Boyle *et al.* (1977), multiple estuaries in the US
		Holliday and Liss (1976), Beaulieu, UK
		Sholkovitz (1976, 1978), Scotland
		Hunter (1983), Taieri, New Zealand
		Yan *et al.* (1991), New Jersey, USA
		Dai and Martin (1995), Ob and Yenisey, Russia
		Powell (1996), Ochlockonee, USA
		Fu *et al.* (2013), Wanquan and Wenchang, Wenjiao, China
		Mulholland *et al.* (2015), Amazon, Brazil
Pb	Non-conservative mixing (removal)	Chiffoleau *et al.* (1994), Seine, France
		Dai and Martin (1995), Ob and Yenisey, Russia
		Wen *et al.* (1999), Galveston, USA
		Waeles *et al.* (2008), Penzé, France
		Tanguy *et al.* (2011), Penzé, France
		Fu *et al.* (2013), Wanquan and Wenchang, Wenjiao, China
		Illuminati *et al.* (2019), Po River plume, Adriatic Sea
Cu	Conservative mixing	Boyle *et al.* (1982), Amazon, Brazil
		Windom *et al.* (1983), multiple estuaries, south-eastern USA
		Shiller and Boyle (1991), Mississippi, USA
		Guieu and Martin (2002), Danube Sulina Branch
		Dai *et al.* (1995), Rhône, France
		Dai and Martin (1995), Ob and Yenisey, Russia
	Non-conservative mixing (removal)	Benoit *et al.* (1994), Texas, USA
		Guieu and Martin (2002), Danube Chilia Branch, Ukraine
		Waeles *et al.* (2005, 2008), Penzé, France
		Illuminati *et al.* (2019), Po River plume, Adriatic Sea
	Non-conservative mixing (addition)	Ackroyd *et al.* (1986), Tamar, UK
		Hunter (1983), Taieri, New Zealand
		van den Berg *et al.* (1987), Scheldt, UK
		Chiffoleau *et al.* (1994), Seine, France
		Guieu *et al.* (1996), Lena, Russia
		Waeles *et al.* (2005), Penzé, France
Zn	Conservative mixing	Holliday and Liss (1976), Beaulieu, UK
		Shiller and Boyle (1991), Mississippi, USA
		Benoit *et al.* (1994), Texas, USA
		Guieu *et al.* (1996), Lena, Russia
	Non-conservative mixing (addition)	Ackroyd *et al.* (1986), Tamar, UK
		van den Berg *et al.* (1987), Scheldt, UK
		Yan *et al.* (1991), New Jersey, USA
		Chiffoleau *et al.* (1994), Seine, France
		Benoit *et al.* (1994), Texas, USA
		Guieu and Martin (2002), Danube, Ukraine

Figure 3. Estuarine mixing behaviour of selected metals, taken from Mosley and Liss (2020)

1.2 Resuspension of sediment

Physical mixing in estuaries involves a dynamic distribution of sediments and suspended matter in the water column and at the riverbed. Sediments are resuspended by wind, tidal and freshwater currents and so, sediment-bound pollutants are remobilized from the riverbed into the water column.

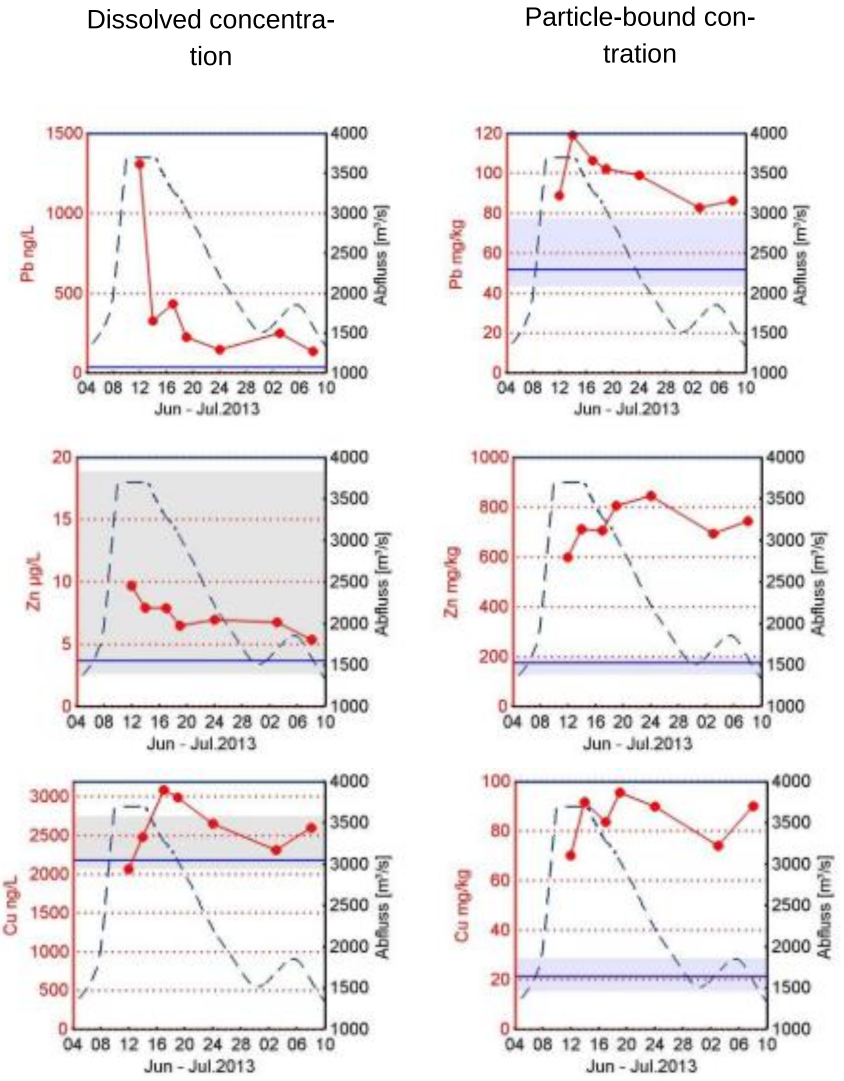
Interactions and redistributions of the estuarine particle matter are a principal aspect to consider when investigating partitioning of pollutants from sampling data. Resuspended matter acts either as a source or sink of pollutants, for instances as a sink when resuspended particles are depleted of pollutants or as a source when they are contaminated. Regarding partitioning, those sinks or sources influence the conservative or non-conservative behavior of a pollutant observed under estuarine conditions, also due to the related porewater release by sediment resuspension that can inject dissolved pollutant into the water column. For instances, in simplified representations of pollutant transport like the linear mixing curve approach (see 1.1), a deviation of conservative mixing can be caused by resuspension of sediments, rather than by a phase-change between the water-solid phases of the pollutant.

During storm surges, unusual amounts of sediments can be remobilized and redistributed in the estuary. In general, storm surges and wind waves are a main driver of shear stresses that induce motion and resuspension of particles from the riverbed of estuaries. Particularly in shallow areas, currents and turbulence induced by storm surges and wind waves have an impact on the sediment transport and as a result, on the particle-bound pollutants.

In a storm surge event, a dilution effect in pollutant concentration is expected through the high marine particle-load transported into the estuary, which is generally clean or barely polluted. That can decrease the immediate effect of remobilized pollutants in the water column. However, little is known about the impact of the redistributed particle-bound pollutant after the storm surge, for example on transferring a source of pollution from one place to another. Also, it is less known about the effect of wind-generated turbulence on polluted sediments settled down in areas of low flow velocities (e.g. groyne fields, harbor basins or foreshore areas).

An increase on the transported water volume that dilutes pollutant loads but also remobilize sediments and pollutants can also occur during large rainfall events and seasonal flooding. Monitoring data in the Elbe basin has shown that very high freshwater discharge remobilizes pollutants stored on the riverbed, inducing an increase in the pollutant concentration that reaches the estuary and overshadows the dilution expected by higher discharges. During the heavy rainfall event in June 2013 at the Elbe basin, the freshwater discharge reached 3500 m^3/s in the estuary, a flow rate more than 4 times higher than the average discharge (Q_{mean} about 700 m^3/s). The remobilisation of accumulated loads was noticeable; heavy metals showed high concentrations during the flood wave by rising waters that decreased by receding outflow waters (Figure 4). The particle-bound metals Lead (Pb), Zinc (Zn) and Cooper (Cu) depicted abnormal concentrations in suspension (particle-bound to SPM), for instances two times higher than reference concentrations (median) and larger than the 10 to 90% percentiles of the years 2010-2012 (Figure 4, right). The dissolved concentrations of Zinc showed in general high variability in comparison to dissolved Cu and Pb (grey band, left), but particulate Zn was found also abnormally high, which can be attributed to the remobilisation of accumulated loads in sediments.

In general, it is expected that at the end of the flood wave of such heavy rainfall events, larger pollutant loads are flushed out from the river catchment, transferring the accumulation of pollutants elsewhere downwards, where for the pollutants, adsorbed or assimilated, settle down again.


Dissolved concentration

Particle-bound contration

Figure 4. Selected heavy metals concentrations measured in Hamburg during a heavy rainfall event in the Elbe estuary in June 2013, taken from BSH 2014.

Flow discharge (dashed line), measured metal concentration dissolved (left), particulate (right). Horizontal bands are reference concentrations available from 2010-2012: median (blue lines) and 10 – 90% percentiles in Hamburg (grey band, left), in the German Bight (blue band, right).

1.3 Retention times

Besides dilution and remobilization of pollutants, physical mixing in estuaries influences the rates of chemical interactions of pollutants with the particles in suspension but also with other water constituents like nutrients and minerals. Large retention times of dissolved pollutants in the water column enhance the likelihood of molecular interactions with other substances or particles in suspension and so, the expected time for them to chemically react.

Retention times can be defined by replacement timescales that calculate the time, freshwater masses or pollutants are renewed or retained within the estuary or sections of it. There are different definitions and concepts of timescales for the study of environmental flows (e.g. residence times, water age, influence, exposure times or flushing times). Following Delhez et al. (2014), residence times measure the time that a hypothetical, dissolved pollutant discharge would need to leave an estuary or part of it. The influence time rather measures the time needed for an initially well distributed concentration to be replaced by 'new' water. Delhez et al. (2014) concluded that for the study of punctual pollutant discharges, the timescales defined by the residence time and water age are more appropriated and for the study of the impact of pollution persistence, the influence times are rather relevant.

The concept of water age is commonly applied in continuous hydrodynamic models to study timescales of the advective-diffusive transport of substances. Holzwarth et al. (2019) calculated the freshwater age in the Elbe estuary by calculating the time that elapsed after a riverine water signal at the tidal barrier entered the estuary. For the flow conditions of 2011 with discharges varying from 400 m^3/s to 3500m^3/s, they obtained water ages that varied between 1 to 25 days increasing from upstream to downstream the Elbe estuary, in strong dependency on the freshwater discharges. For the highest discharges in January the smallest riverine ages were reported.

This evidenced that transport timescales like the water age (or for instances the residence time) are ruled by the flow currents resulting mainly from tidal forcing and freshwater discharge, thus, the modelling performance of the hydrodynamics in estuaries is central to account for natural variations in retention times like for instances through spring and neap tides, storm surges, and low and high freshwater discharges in summer and winter. For the diagnostic of pathways of the pollutants and the potential reactivity with other particles that plays an important role.

Morris (1990) discussed the estuarine chemical reactivity within an one box model. He compared estuary size, chemical time constant (half-life) of trace metals, and freshwater replacement times as a parameter for physical mixing. He showed that for sorption and desorption of trace metals to occur, the time available for the reaction within the estuary has a major effect. Together with the half-life time constant of the investigated trace metals, the hydrodynamic replacement time determines whether the partitioning of trace metals can be assumed to behave conservative (linear mixing curve), in a kinetic range (non-conservative behavior), or in equilibrium (Morris 1990).

1.4 Vertical mixing and particle interactions at small scales

Vertical mixing induced by turbulence affects the transport of pollutants in many senses. One major consequence is the resuspension of sediments near the riverbed, which can bring in motion pollutants, adsorbed onto the sediment-surface or stored in pore waters, into the water column (see 1.2). Furthermore, particle interactions promoted by turbulent vertical mixing have a key role in the vertical distribution of pollutants. By high tidal shear stresses and high waves currents, turbulent motion propagates along the water column, whirling up water and SPM, increasing dispersion and the likelihood of collisions between particles and flocs in suspension.

Flocs are aggregates with low density that consist largely of inorganic clay and water, bound together by mucopolysaccharide (Fitzsimons et al. 2011). The formation and disruption of flocs is of relative importance because they can remove dissolved pollutants from the water column in aggregated small size-particles, but also because they can release pollutants from the floc matrix to the water column as they disaggregate. Due to the small sizes of the aggregated particles (e.g. clay size < 4 µm), they provided more sites for adsorption than coarser particles, i.e. they have large specific surface areas (SSA).

The vertical dynamics of small particles due to formation and disruption of flocs is principally ruled by the intensity of the bed shear stress induced by flow currents. Along a tidal cycle, floc formation has been observed during slack water, where the shear stresses are the lowest. Floc disruption seems to occur around mid-tide, where the flow currents and shear stresses reach maximal values. In the turbidity maximum zone (TMZ), the smallest median particle-size have been observed at the greatest tidal shear stresses, suggesting the disaggregation of flocs (Fitzsimons et al. 2011). That sorting of particle-sizes can redistribute pollutants adsorbed to the finest and colloidal-size particles in the water column.

Measurements in the Humber (UK), Tamar (UK), Mersey (UK) and Elbe (GE) estuaries showed that the decrease on particle size in SPM observed in the TMZ coincided with an increase in the specific surface area (SSA) of the suspended solids (Millward et al. 1990). Either because of floc disaggregation or particle selection, the SSA was found to reach a maximum in the TMZ involving colloidal sized particles. Hereby, the highest SSA was measured at the Elbe estuary.

Colloids are small particles with large SSA and therefore strong sorption capacities (Fitzsimons et al. 2011). Their size is smaller than 1µm (Mosley and Liss 2020) and even when their particle-size overlaps the size-range of operationally defined dissolved fractions (< 0.45 µm in the Elbe estuary), colloids exhibit the physicochemical properties of a solid. The SSA together with the charge of the surfaces (normally negative because of an enveloping film of organic matter) makes them a major carrier for particle-bound pollutants such as trace metals. The aggregation of colloids is first driven by coagulation as increased seawater cations mix with freshwater and neutralize repulsive forces that hold the particles in suspension. Followed by the attraction exerted by Van der Waals forces, particles aggregate to flocs, for instances, in regions of low shear stresses (Fitzsimons et al. 2011; Mosley and Liss 2020). Mediated by the settling-down of the particle-aggregates, adsorbed pollutants are removed from the water column. The transition between physical and chemical mechanisms (coagulation and flocculation) is fluent. According to Mosley and Liss (2020), in particular the heavy metals Cu and Zn tend to bind to the colloidal fraction. The speciation of these metals with colloids is discussed in section 3.

Nevertheless, the mechanisms inducing flocculation have not been completely understood and about the quantitative role of flocs in the distribution of pollutants little is known. Alone the observation of flocs behavior in estuaries is challenging because flocs are fragile, and in situ measurements are affected by the analysis procedure, sampling technique and sampling timing considering that tidal currents makes them to change in size and shape during a tidal cycle (Fitzsimons et al. 2011).

2 Influence of physicochemical conditions on pollutant distribution

Physicochemical conditions that typically vary in estuaries influence the thermodynamic drive for particle-water interactions in the water column as well as the speciation and reaction rates of chemical constituents. Changes on the pH-value, temperature, salinity and organic matter occur in time and space for instances with sharp gradients.

Salinity increases with distance from the upper estuary to the mouth in ranges around 0 to 32 (practical salinity scale) in the North Sea region. Besides this spatial variation, salinity intrusion (saltwater limit at the fluvial riverside during flood) varies also seasonally: by low freshwater discharges, brackish water is shifted landwards into the estuary and by large freshwater discharges brackish waters are displaced seawards.

The spatial gradient in pH and temperature is less pronounced than salinity, at least in well-mixed estuaries, but seasonal changes are evident. At the Elbe estuary, the pH varies from 7.5 to 9[1], the highest pH-values occur in summer due to the bicarbonate assimilation of phytoplankton (i.e. the uptake of inorganic carbon as a source for photosynthesis). The variation of water temperature (average day temperature) in Hamburg can rise more than 20 °C between summer and winter months.

According to Fitzsimons et al. (2011), the amount of particulate organic carbon (POC), a main constituent of organic matter, varies from about 1% to 25% dry weight of SPM in European Estuaries. In the water body of the Elbe estuary, the organic matter content varies the most in the upper estuary since there, the river is fluvial dominated and thus, seasonal influenced by algae blooms during spring and fall. The organic matter content can constitute until 50% of the SPM in the upper estuary (BfG 2008). Most of the organic matter (phytoplankton) that enters the estuary thorough freshwater is rapidly degraded in the upper estuary (Hamburg area of the estuary). However, sampling timing, depth and location can be relevant to notice seasonality on the organic matter content. TOC determined during 1985 and 1998 from samples near to the water surface (6 to 7 samples per year) did not evidenced pronounced seasonal variation at the fluvial riverside of the Elbe estuary in the monitoring measurements of ARGE 2000. The TOC at approx. 0.5 m bellow water surface varied between 1.6 and 50 mg/l C along the tidal river (ARGE 2000). In the turbulent maximum zone, high values of particulate organic carbon POC stood out, most probably due to high SPM concentrations (ARGE 2000).

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[1] Monitoring data since 2002 published on https://www.fgg-elbe.de/files/Download-Archive/Gewaesserguete/Schnellberichte%20Befliegung_ab_2014/230213_Schnellbericht_Befliegung.pdf

In the following, the influence of the above-mentioned estuarine variations on pollutants transport collected from different studies in North Sea estuaries is discussed.

2.1 Salinity

The partitioning of pollutants like heavy metals is expected to be influenced by salinity due to the increased influence of seawater ions that either compete with metal ions for sites on the particle-surfaces, or attract the particle-bound metals to form complexes in water-phase. Both mechanisms lead to metals desorption. Besides causing desorption, seawater ions destabilize permanent suspended matter and induce coagulation, so that particle-bound pollutants drop with the formation and settling down of flocs (see 1.4). In this manner, a decrease on the particulate concentration of the pollutant could be observed dominated by the vertical transport of carrier particles.

Desorption of particle-bound metals with increased salinity, for instances for Cd, has been attributed to complexation with chlor-compounds dissolved in seawaters. The adsorbed metal onto the particulate surface can be susceptible to form stable complexes with dissolved chlor-compounds, which induces a phase change, from the particulate to the dissolved phase.

Turner (1996) proposed an equation to model partitioning, by estimating the partition coefficient K_D in dependency on salinity and the relative proportion of a resuspended particle fraction with respect to a permanent SPM fraction. With the two fractions, it should be considered that resuspended and permanent SPM can have different adsorptive capacity. The application of this equation showed good correspondences with the K_D-values acquired from measurements at the Weser estuary. In other estuaries like the Tamar at mid-estuary the estimations were less successful, as he argued, probably due to extraneous influences (anthropogenic, tributary and pore waters), and due to the short water residence times of the Tamar estuary (7-12 days) against the up to 50 days at the Weser estuary that allow chemical equilibrium between dissolved and adsorbed species to be approached. Furthermore, the equation strongly simplified sediment and SPM transport by considering only two particle fractions that invariantly traverse the estuary, so that the results might be also limited by the simplified transport of different particle-sizes.

In contrast to heavy metals, organic pollutants might be subject to enhanced sorption with salinity rather than desorption as described above. This is because the salting out of neutral compounds, when seawater ions compress water-molecules so they become better aligned with each other and other neutral molecules such as organic pollutants are forced out of the solution. Then, the solubility of organic compounds decreases (Turner and Millward 2002).

Besides the salting out effect of dissolved organic pollutants, Turner and Rawling (2001) showed that increased partitioning of neutral organic compounds with salinity was as well accounted for by the stabilizing effect of seawater on the organic matter surfaces. They concluded that as seawater cations neutralize the negative charges of the organic matter (and possibly modify the structure of the organic matter), also the particle-bond of neutral organic compounds is enhanced. Thus, the effect of salinity in decreasing the solubility of neutral organic compounds is accompanied by changes on the SPM surfaces, for instances of the organic matter coating charges, due to interactions with seawater ions.

2.2 Organic matter

It has been demonstrated that the distribution of heavy metals is strongly affected by the abundance of colloids and small particles that consist of inorganic and organic matter (see 1.4). In general, inorganic particles as clay and silt can bind fine organic particles due to organic mineral complexation (CIS 2022).

In natural rivers, an organic coating that envelops particles in the water column is ubiquitous, independent of grain-size or elemental composition. The organic coating is normally negatively charged, due to dissociated functional groups (e.g. COO^-) (Mosley and Liss 2020). Following that, the particle interactions of (at least) the riverine fraction in SPM are controlled by the organic film on the particle surface, where the SPM is a mix of riverine particles, resuspended particles with larger retention times and marine particles (besides other inputs from anthropogenic or terrestrial loads within the estuaries). Changes on the composition of organic matter are caused in estuaries by the biological activity of plankton and bacteria. The release of transparent exopolomeric particles (TEP) by phytoplankton has been found to enhance flocculation (Mosley and Liss 2020). Winterwerp et al. (2002) argued that OM might also affect the size and structure of flocs.

The influence of organic matter (OM) on particle-binding of heavy metals has been reported for Cu and Zn. In estuarine conditions, the bond of Cu and Zn to organic species including colloids has been reported for example in the works of Wang and Wang 2016; Mosley and Liss 2020. Also in 3D-modelling approaches, OM has been considered as a metal-carrier in the suspended phase (Li et al. 2010).

Seasonal changes on the distribution of heavy metals and organic pollutants can be associated with the particulate and dissolved organic matter cycle, when the pollutant is adsorbed or bound to organic matter. However, transport models, for instances for metals, typically derived the partitioning either with respect to the SPM concentrations (principally made of inorganic particles) or to fractions of clay and silt, but changes on organic matter content in SPM were not considered. One reason for that might be the difficulty of modelling the dynamics of organic matter in sediment transport models since established sedimentological models characterize the transport of SPM and bedload by means of physical meanings, i.e. by the hydrodynamics, density and settling velocities of the inorganic particles in suspension without solving the associated organic matter dynamic.

For persistent organic pollutants (POPs), sorption to organic matter is the dominant transport mechanism due to the preferred hydrophobic interactions of POPs. Organic matter (OM) is the primary sorbing constituent that carries particle-bound POPs in estuaries. Since the composition of OM varies (e.g. polarity and aromaticity), the partitioning of the same pollutant to OM might vary depending on the environmental conditions; for example, where the fluvial influence is dominant and humic acids in OM are relative high, the binding on OM increases by the complexation of metals with humic acids (Fitzsimons et al. 2011).

Organic matter is dynamically transported between water and SPM and operationally defined as dissolved (DOM) and particulate (POM) according to filtrate and filtered residue through pore sizes between 0.22 to 0.7 µm. Both organic pools POM and DOM behave in estuaries non-conservative, subject to phytoplankton production and degradation by microbes and larger organisms. The OM transformation, for instances from the particulate pool POM to the dissolved pool DOM should influence the distribution of pollutants adsorbed to POM, as carried POPs undergo the OM transformation and phase change.

2.3 Other parameters

Chemical interactions arise also due to the presence of iron and manganese oxyhydroxides, which are common mineral colloids in estuaries. It is established that the precipitates of iron and manganese oxyhydroxides can bind pollutants in the particulate phase since those oxyhydroxides exhibit relatively high specific surface areas (Balls 1989; Singh et al. 1984; Fitzsimons et al. 2011).

The redox-state of the water column and sediments also influence the speciation of some metals (Moesly, 2019). Changes on the redox balance might occur for instances by upwelling and whirling up the surface layers of the bed loads stored in anoxic or sulfide conditions. Then, oxygen get in contact with the pollutants stored in reduced conditions and this can enhance the mobility of the pollutants. It is known that under anoxic conditions, pollutants are less biodegradables (Chiaia-Hernández et al. 2022). Following resuspension, mobilized pollutants can also interact with water constituents dissolved or permanent suspended in the water column, and change the partitioning conditions.

Changes on the physicochemical conditions in the estuary are also controlled by biogeological drivers, therefore, some biological processes can affect the distribution of pollutants. In particular, regional and seasonal patterns in pollutant concentration are characterized by biogeochemical conditions. For instances, the carbonate assimilation by phytoplankton changes SPM composition and pH conditions; the uptake of inorganic carbon by phytoplankton for photosynthesis shifts the pH-values to more basic conditions and can induce precipitation of calcium carbonate, diluting the concentration of the metals in the particulate phase (Pepelnik et al. 2004). Also adsorption to biota and biogeochemical process can lead to a attenuation of pollutants pulses that cannot be alone explained by dilution (Chiaia-Hernández et al. 2022).

3 Speciation of selected pollutants

The mobility and sorption of a pollutant is mediated by the chemical form (specie) that the pollutant adopts being exposed to seawater ions, oxyhydroxides, pH-conditions or variable organic and inorganic particles. The suspended and dissolved matter, present in the water column, interact with the pollutant depending on the chemistry of the pollutant itself, for instances depending on its electrical charge (i.e. positive for metal aqua ions and neutral for several organic pollutants).

With changing water constituent conditions like pH, salinity and minerals, different chemical properties of the pollutant determine whether it is adsorbed, desorbed, volatilized or complexed with other molecules.
A compilation from different studies about the speciation of the heavy metals Cu, Zn, Cd, Pb and organic pollutants HCB, DDx and PCBs observed in estuaries and coastal waters is in the following presented.

Heavy metals:

Cadmium (Cd):

Cd is known to have a strong affinity to inorganic matter like carbonates and clays but also to organic matter content. Similar to the general behavior of metals, Cd is expected to be rapidly adsorbed when released in natural rivers. The partitioning might occur within minutes, resulting in a fast removal of Cd from the water-phase, followed by a slow desorption, within weeks, until it reaches stable concentrations (chemical equilibrium) in the solid-water phase (Layglon et al. 2022).

In the Elbe estuary, Cd was found about 60% to 90% particle-bound in suspension (Prange 1997). A rapid decrease on the particle-bound phase has been observed downwards of the turbidity maximum zone (TMZ), and in the North Sea, Cd is found principally dissolved (BSH 2014).

It is established that complexation is a relevant influencing factor affecting the speciation of heavy metals with salinity, in particular the speciation of Cd. Cd complexes are stable chemical species in solution that might prevent the metal sorption onto particles surfaces (Artiola 2004). So, the partitioning of Cd is lessened and its transport in dissolved form enhanced.
The seawards decrease of the particle-bound Cd has been attributed to the formation of high stable and soluble chlorocomplexes (Turner et al. 1993).

Zink (Zn) and Copper (Cu):

The speciation of Cu has been related to organic matter, in particular with the colloidal and dissolved organic matter content (DOM). According to Mosley and Liss (2020), 99% of Cu found in estuaries (and natural rivers) is bound to an up to now unidentified organic ligand or group of ligands present at low concentrations. In general, Zn and Cu have been proofed to be stronger influenced by colloidal-ligands than Cd (Mosley and Liss 2020).

Sediment-bound Cu was found associated to mobile phases with Fe and Mn hydroxides or to the organic/sulfidic phases in the port of Gothenburg during a study from 1994-2000, suggesting that the Cu content preceded from anthropogenic sources (H-SENSE 2000); the same study reported at the Ventspils harbour that Cu and Zn poorly correlated with aluminum, when comparing the sediment concentrations of Cu and Zn with those of Al (Al is used as a reference for Alumosilicate characteristic for clay). On the other hand, they correlated more with each other and with the concentrations of Mg and Fe. Their findings were interpreted as signals of anthropogenic contamination signals[2].

Regarding the speciation in the water column, the works of Prange (1997) in the Elbe depicted that Cu upwards the turbidity maximum zone (TMZ) is transported equivalently in solution and in particulate phase: in the mid-estuary, under relative low SPM concentration, about 20% of the total Cu per liter water was particle-bound transported, whereas the highest particulate contributions (about 80%) were found in the TMZ due to increased SPM content. This indicates that both compartments are relevant in calculating the total loads of Cu transported along the estuary. Zn depicted a higher affinity to the particulate phase in suspension; the particulate Zn transported along the estuary varied between 60 to 90% with respect to the total Zn load per liter water. Similar to Cu, the highest concentrations per liter water of particulate Zn were found in the TMZ. Downwards of the TMZ, the particulate Zn sharply decreases. According to Prange (1997), for the estimation of the total transported loads of Zn, the dissolved phase remains relevant.

Lead (Pb):

In the study of H-SENSE 2000 at the Gothenburg port, more than 50% of the sediment-bound Pb was found in mobile phases (bound to Fe and Mn oxides or to the organic/sulphidic phase); a correlation of Pb with TOC or particle-size was not found. The authors suggested that the mobile binding of Pb to sediments was an indication for larger anthropogenic Pb sources than natural ones (H-SENSE 2000). Similarly, in the Ventspils Harbour, Pb in sediments poorly correlated with Aluminum, organic matter or other metals (with exception of Cu). There, the variation of the sediment-bound Pb were moderated in comparison to the distribution of other metals (H-SENSE 2000). Pb seemed to be predominantly influenced by other factors not related with the distribution of fine particle-sizes (poorly correlation to Al as a marker of Alumosilicate present in clay).

In the Elbe estuary, Pb in SPM has been found to be principally transported bound to particles (> 90%) (Prange 1997). Towards and within the TMZ, the particulate and total concentrations rose, followed by a rapidly decrease downwards of the TMZ.

Besides the particulate and dissolved loads into estuaries, measurements of metals in the surface waters of the North Sea indicated the relative importance of atmospheric metal loads as a pollution source, particularly for Pb. The concentrations of Pb (among other trace metals) at the water surface were found higher than the concentrations at depth; it has been argued that Pb held on atmospheric particles is desorbed and inserted in the water column, when it gets in contact with seawater (Millward et al. 1998).

For all four metals Pb, Cu, Zn and Cd, the works of Prange (1997) let inferred that the vertical transport in the TMZ through mixing, resuspension and deposition, as well as the increased

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[2] For the interpretation and transfer of these speciation results, the specific environmental conditions should be considered, for instances salinity, which is much higher in the North Sea than in the Baltic sea.

salinity and retention times towards TMZ are factors of relative importance for the partitioning behavior in the Elbe estuary.

Persistent organic pollutants (POPs):

Several organic pollutants are characterized by being neutral charged and high lipid soluble, for instances chlorinated compounds as dichlorodiphenyltrichloroethane (DDT), hexachlorobenzene (HCB) and polychlorinated biphenyls (PCBs). Those favor hydrophobic interactions, which enhance their tendency of being adsorbed and bioaccumulated by biota.

The principal adsorbent of organic pollutants in the water column is in general organic matter. The speciation on particulate and dissolved organic matter is therefore more relevant for neutral organic pollutants than for other polar pollutants like heavy metals.
The high SPM content of the TMZ is in general accompanied by an increase on dissolved organic carbon (DOC). Thus, towards the TMZ, DOC might increasingly compete with constituents of SPM in binding organic pollutant and eventually shift the partitioning ratio to lower values. On the other hand, resuspension of polluted sediments that reached equilibrium with the pollutant concentration in pore waters (e.g. bound to DOM) might inject pollutant loads in both water-solid phases in the water column. Therefore, DOC can act for instances as a source or as a sink of POPs in the water column.

POPs are transported both, adsorbed and dissolved through the environment compartments water, SPM and sediments, but also thorough the air. Atmospheric pathways can represent pollutant sources or sinks because several organic pollutants are semivolatile. Either in vapor phase or adsorbed on atmospheric particles in solid phase, they are released in estuarine and coastal waters (Fitzsimons et al. 2011). Very persistent pollutants like polychlorinated biphenyls (PCBs) might be not decomposed or volatilized within the time span they are retained in the estuary, however, studies in the Kattegat sea showed that oversaturation in water of PCBs led to volatilization (R.W.P.M. Laane et al. 2011).

Other chlorinated pollutants like DDT might be degraded to a certain extent under estuarine conditions, i.e. through changes on temperature, pH and redox conditions. For instances, degradation of DDT to Dichlorodiphenyldichloroethylene (DDE) occurs principally in presence of oxygen, whereas in a reducing environment, the degradation from DDT to dichlorodiphenyldichloroethane (DDD) predominates.

In terms of partitioning, the speciation of organic pollutants might be influenced by salinity (see 2.1). It has been shown that the solubility of nonpolar or weak polar organic compounds is lower in seawater. This so-called salting-out effect can result in an increase on partitioning, however, the relevance of this process has been argued to be debatable due to the uncertainties in partition coefficients (R.W.P.M. Laane et al. 2011).

4 Partitioning in water-solid phases through numerical modelling

In estuarine natural waters, the application of fundamental theory for chemical reactions remains often limited to a qualitative understanding due to the variety of particle-water interactions with physical, biological, electrostatic and hydrophobic effects (Fitzsimons et al. 2011). The mixing and particle-bound behaviour of metals in estuarine and coastal waters has been quantitative described principally as a consequence of the hydrodynamic drive and sorptive exchanges.
In a water-solid phase-system, the total concentration of a chemical constituent strives a thermodynamic equilibrium between the dissolved concentration in water and the concentration adsorbed on the surfaces of particles. Approximations to model the partitioning of pollutants assume in general chemical (quasi-) equilibrium. This is expressed by the partition coefficient K_D, the ratio between adsorbed and dissolved concentration, which varies in dependency on several environmental factors in natural waters.

1 Partition coefficient (K_D): Ratio between particulate concentration (P) and dissolved concentration (C) at chemical equilibrium

$$K_D = \frac{P}{C}$$

In the 1980s and 1990s, extensive measurements and investigations started to describe the partitioning behaviour of trace metals in estuaries at the North Sea: in the Weser estuary (GE), Turner et al. (1992) demonstrated the non-conservative behaviour of dissolved metals due to sorption-reactions and illustrated the variation of the particle-bound metals caused by physical mixing. In the Humber Estuary (UK), batch mixing experiments depicted the removal of particle-bound metals caused by the salinity gradient: the particle-bound concentration of cadmium (Cd) in SPM was about three times higher at a salinity of 1.7 (in freshwater) than downstream at a salinity of around 30.8 as a result of the complexation of Cd ions with chloride ions that mobilized particle-bound Cd to dissolved Cd at higher salinity (Turner et al. 1993). In the estuaries of Rhine (NE), Hudson (USA) and Tamar (UK), Turner et al. (1993) obtained similar results, but the estimated partition coefficient K_D varied from estuary to estuary. Measured K_D-values can be difficultly transferred from one location to another (Balls 1989) since the biogeochemistry and hydrodynamic forces in different estuaries are rather heterogenous. Furthermore, the partitioning represented by K_D ascribed a seasonal variation for many pollutants, and therefore, a variation in time, as demonstrated in studies at the tidal Elbe for trace metals and organic pollutants by Prange (1997) and ARGE (1998).

The concept of the partition coefficient K_D as an empirical parameter has been extensively used for modelling trace metal distribution in natural waters based on estuary-specific sampling data. In simple mechanistic equilibrium chemical models, the K_D-parameter is determined by measurements and incorporated into the models, for instances, as a constant parameter, as a function in dependency of SPM (Turner et al. 1992), of salinity (Turner and Millward 1994), or both, salinity and SPM (Turner 1996). Those K_D calculated within simplified mass balance models (box-models) differs from the K_D coefficients that might be required for a numerical transport (hydrodynamic) model that resolves sediment transport, in particular when the vertical transport of particles in the water column is resolved (e.g. in 3D).

On the other hand, chemical models (without transport modelling) might be able to predict observed K_D-values, like for instances referred by Fitzsimons et al. (2011) for Zink in the Humber estuary with the models WHAM and SCAMP. Those models consider the chemical heterogeneity of natural particles (oxides, fluvic and humid acids) that react with pollutants and simulate the chemical changes in metal partitioning in equilibrium and the speciation of pollutants (Fitzsimons et al. 2011, p. 102). Tappin et al. (1995; 2008) came to the conclusion that to model trace elements in the North Sea, model approaches accounting for both hydrodynamics and geochemistry are needed. However, acceptable accuracy with high levels of complexity in hydrodynamics and geochemistry might be difficult to solve at the same spatial and time scales; the spatial scales needed to resolve chemical processes are at molecular-level, whereas those relevant for the solution of estuary hydrodynamics are at much larger meso-scales. Parametrizations of fine-scaling process are the common method to build up the geochemical interactions of pollutants in transport modelling-systems, that resolve the hydrodynamics at estuarine scales (from m to km). Transport-chemical coupled models make use of the K_D parameter to parametrize the partitioning due to sorption, desorption but also precipitation and complexation. Those perform primordially the hydrodynamics and sediment transport (with adequate accuracy), which are responsible, besides partitioning, for the transport of pollutants in the water-solid-phase system.

More recently, investigations have linked the partitioning of heavy metals also with the variation of organic matter content, for example regarding the seasonal distribution of Cd, Co, Cu, Mn, Ni, and Zn (Briant et al. 2021), the complexation of Cu with dissolved organic matter (Gaulier et al. 2021; Mosley and Liss 2020) or sorption of Pb to POC (Li et al. 2010).
Biological driven processes regarding primary production and degradation of OM are in particular significant for the partitioning of persistent organic pollutants (POPs) because its primary sorbing constituent is OM. For POPs, partitioning can be represented by the coefficient K_{oc}, which is K_D normalized to the content of particulate organic carbon POC ($K_{oc} = K_D/[POC]$) (Fitzsimons et al. 2011).

Biogeochemical models have been applied to simulate the pathways of organic pollutants, using POC as a non-conservative pollutant-carrier, produced and degraded by biological processes (Daewel et al. 2020). Often, biogeochemical models are fed with the outputs of hydrodynamic models, to account for the spatially time-depending distribution of the concentrations. In contrast to multimedia models (also called box models), coupled biogeochemical–hydrodynamic modelling systems can represent the gradients of the concentrations of water constituents in 3D resolution (Holzwarth and Nickelsen 2019). However, those approaches significantly enhance the complexity of the solution, solving predominantly the biological processes related to oxygen concentrations, focusing less on the turbulent, density-dependent transport of OM, which is relevant for the fate of pollutants. Generally, the coupled transport of OM and inorganic sediments is neglected or uncoupled considered, because the physical behaviour of OM in sediment transport for instances in flocculation or turbulent mixing is difficult to characterize, in fact, this is subject of current research. Efforts to parametrize the organic matter in sediment transport models are for example found in the studies of Maerz and Wirtz 2009; Schartau et al. 2019; Fettweis et al. 2022.

When different sorbing constituents of OM and inorganic matter are built in transport fate models, a specific K_D coefficient has been used to represent the affinity of each constituent to a specific pollutant; for instances a different K_D might be defined for silt, clay, colloids (different particle-sizes), phytoplankton, POC and DOC (Wang and Wang 2016; Mosley and Liss 2020; Deltares 2022; Fang and Wang 2022). In the partitioning approach, it is assumed either chemical equilibrium (K_D is constant), or sorption kinetics are computed, solving i.e. first order reactions.

To represent the effect of increased seawater ions on the partitioning of trace metals, Turner (1996) proposed a function of K_D in dependency on salinity within a mass-balance model. Similar dynamic formulations of K_D considering salinity have had less application in numerical transport models. However, it is established that salinity can enhance the affinity of metals to the dissolved phase by competing and complexing seawater ions, besides other effects on metal speciation due to the increased ionic strength (Mosley and Liss 2020). Other potential factors affecting metal behavior like pH, metal oxide surfaces, inorganic and organic complexation have not been integrated in transport models, which might be able to forecast the distribution of pollutants in estuaries (Mosley and Liss 2020).

5 Summary of knowledge gaps and future developments

This work provided a concise review about relevant processes in dynamic estuaries like the Elbe estuary that potentially influence the distribution and transport of pollutants at estuarine scale. The representation of those processes by means of the K_D-concept was discussed, a concept that has been extensively employed in modelling to represent partitioning of particle-bound reactive water constituents.

Mixing processes and variable physicochemical conditions have an effect on the distribution of particle-reactive pollutants in different spatial and time scales. The mechanisms causing changes on the concentrations of the pollutants like dilution, partitioning and complexing are known in general, however the relative importance of each process at estuary scales is difficult to measure in-situ, and it is site-specific. For instances, the significance of dilution in decreasing particulate pollutant, depends on the environmental conditions of the estuary like the location of the estuarine transition zone (ETZ,) extension of salt intrusion, and tidal and turbulent energy steering physical mixing within the system. On the other hand, dredging and relocation of sediment in estuaries like in the Elbe are a continuous influencing factor that also alter the mixing conditions in the water column.

In numerical experiments, the segregation of those effects acting simultaneously is a main advantage for understanding and describing pollutants transport. For that, accurate parametrizations of the sediment dynamics are indispensable. Sediment transport models in 3D provide a good resolution of physical mixing in the water column, nevertheless, flocs formation and disaggregation as well as the effects of organic matter composition on flocculation are not well understood, and required further research. In particular, parametrizations of the organic matter in sediment transport models are needed to model the transport of pollutants that are predominantly adsorbed by OM.

The partition coefficient K_D has been less studied in numerical hydrodynamic transport models in dependency of variable estuarine conditions like salinity or organic content, those are known influencing factors affecting the partitioning of heavy metals and POPs. Further research is here required to integrate K_D parametrizations in numerical hydrodynamic transport models that reflect the K_D-dependency on variable estuarine processes to simulate the transport of legacy pollutants with improved accuracy at estuary-scale.

Modelling forecast and hindcast studies regarding pollutant transport and distribution are indispensable to develop sustainable measures in estuaries affected by sediment pollution, for instances to design remediation measures in highly contaminated areas, to assess the ecological risk of sediment management activities, but also to assess the effects of storm surges and extreme freshwater discharges due to climate change causing the remobilization of pollutants.

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Signed,

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