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Sediment water (interface) mobility of metal(loid)s and nutrients under undisturbed conditions and during resuspension

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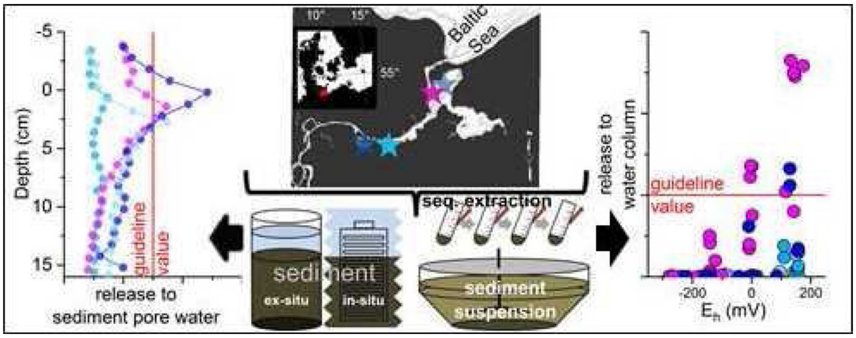
GRAPHICAL ABSTRACT



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ABSTRACT

The contribution of the release from sediments to the overall river Trave budget was evaluated with respect to 16 metal(loid)s, three non-metals and the ions PO_4^{3-} and NH_4^+. To consider undisturbed conditions and sediment resuspension *in-situ* dialyses-based and *ex-situ* suction-based pore water sampling was complemented by sequential extraction and suspension reactor experiments. In the investigated sediments, representative for the study area, metal(loid) partitioning between the different geochemical fractions was very similar despite some higher contaminated spots. Pore water investigations emphasis that profiling and peeper based analyses are comparable and deliver an indication that sediment dwelling organisms are exposed to elevated metal(loid) concentrations. However, higher toxicity of the contaminated sediments compared to the sediment treated as background reference was not revealed. During resuspension only few metal(loid)s exceeded specified guideline values. The maximum amounts released, were only between 10^{-5} and 10^{-1}% of the average daily load of the river Trave per ton of suspended sediment. Overall the "most pristine sediments" and not the potentially hazardous materials in the study area are found to be from highest concern. The results support requests to better include fractionation and speciation demands in legal assessments of sediments.

1. Introduction

The environmental risk posed by contaminated soils and sediments remains to be often estimated by methods based on the total contaminant content. However, many elements are only partially bioavailable due to their specific chemical properties and prevailing

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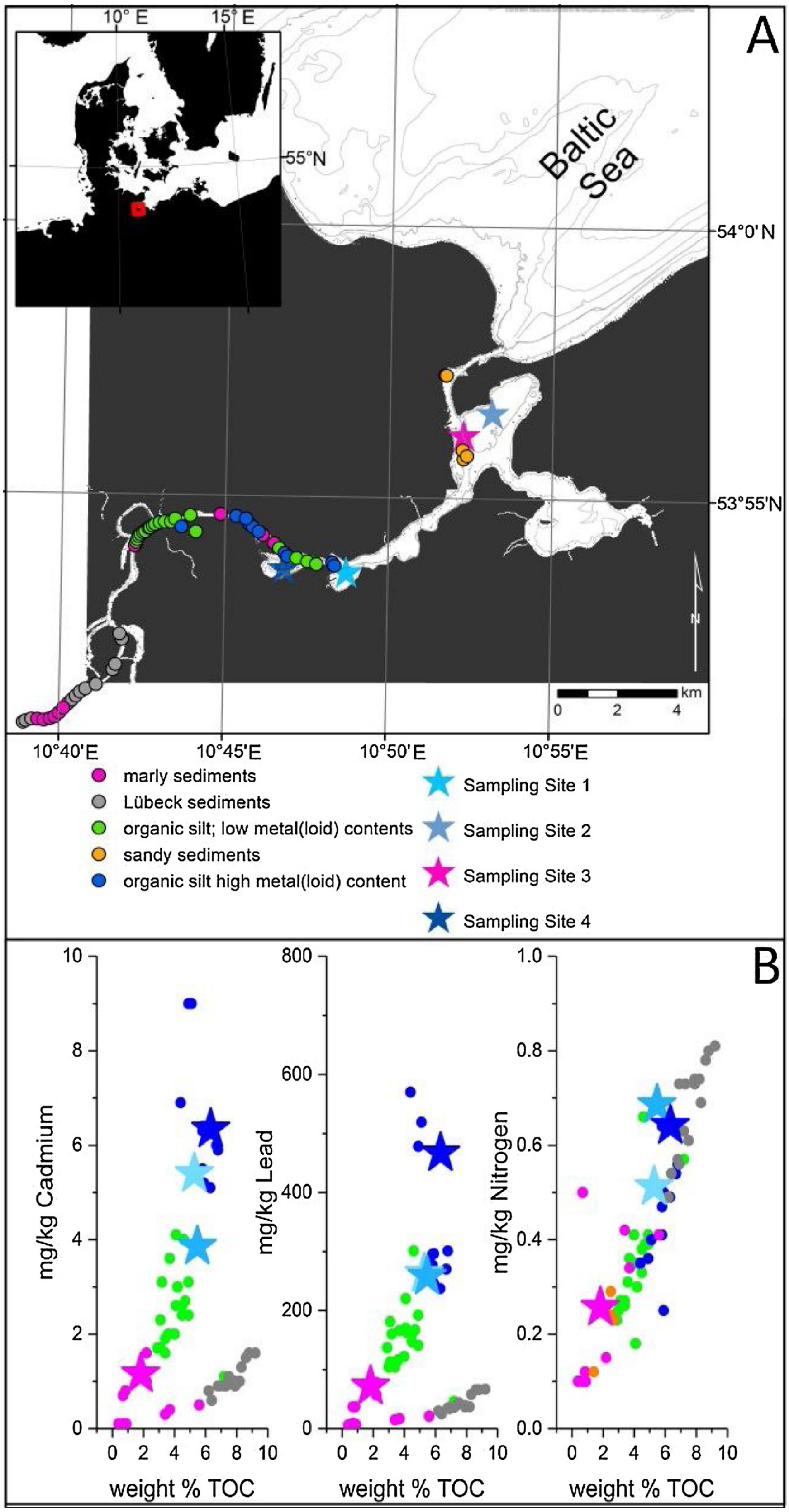

Fig. 1. Sediments of the Trave estuary and examined sampling sites. a) Location of sediment samples provided in SedKat and examined sampling sites in the Trave estuary. The coloring represents the results of hierarchical cluster analysis. b) Cadmium, lead, and nitrogen of samples located in SedKat and examined sediments plotted against their TOC content. The coloring represents again the results of the cluster analysis (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

environmental parameters (Eggleton and Thomas, 2004; Vink, 2009). Therefore, it is generally accepted that mobile fractions $< 0.45\,\mu m$ operationally defined as dissolved provide a more significant measure to describe potential adverse environmental effects for many contaminants including metal(loid)s (Schafer et al., 2015; Mayer et al., 2014). In this context mechanical disturbance of sediments by human activities (e.g., construction and maintenance activities in waterways) or from natural causes (sediment dwelling or sediment slides) are of interest. Thus, the availability and release of pollutants both from deposited and from suspended sediment needs to be considered. Approaches that evaluate sediments, based on mobile concentrations (dissolved in pore water) have been developed for a limited number of contaminants (U.S. EPA, 2005). However, steep gradients of environmental parameters prevailing at the sediment water interface (SWI) and the typically resulting steep concentration gradients of metal(loid)s in particular in the dissolved fraction are usually not (sufficiently) considered. This is partly due to constraints associated with different available sampling techniques such as the affection of sample properties and analytes speciation, missing spatial information (e.g. squeezing and centrifugation) or the need of long exposure times (e.g. diffusive gradients/equilibration in thin film (DGT/DET)). With the mesoprofiling and mesosampling system (*messy*) the authors recently introduced techniques for low-invasive, high spatially resolved pore water sampling (Schroeder et al., 2017, 2019) capable to overcome some of these limitations. When working with disturbed samples, the release remains to be often estimated based on fractionation concepts by (sequential) extractions, which are also used in regulation worldwide. With respect to the changing conditions, “dynamic” bio-geochemical microcosm experiments (Yu and Delaune, 2013; Yu and Rinklebe, 2011), offer additionally to the “static” (sequential) extractions, the opportunity to study the release of metal(loid)s from sediment suspensions, while manipulating environmental key parameters such as redox potential (E_h) and pH value.

State of the art analytical techniques deliver the opportunity to easier expand the set of analytes beyond the few potentially toxic elements (next to organic pollutants) considered in standardized risk assessment procedures. Further potentially toxic elements as well as elements acting as important sorbents or reactants can nowadays be included in a single analytical run.

To describe the potential contribution of the sediment release to the overall metal(loid) and nutrient mobility the Trave estuary (German Baltic Sea coast) was chosen as study area, owning an intensive history of pollution and strongly impacted by the management (water way maintenance). Four different approaches were combined to address the mobile fraction from four sampling sites investigated. The sites were chosen by feature, characteristic for the estuary with respect to physicochemical properties and the relocation potential. Operationally defined as dissolved concentrations of the 16 metal(loid)s Ag, As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sb, Se, Sn, V, Zn, the non-metals C, P and S as well as the ions NH_4^+, PO_4^{3-} and SO_4^{2-} were examined. Therefore, the mobility of the analytes at the SWI *ex-situ* using a high resolution suction-based pore water sampling, was compared to peeper based *in-situ* sampling (all sampling and installations were undertaken by scuba divers), complemented by sequential extraction following the BCR (Community Bureau of Reference, European Commission) Ure et al. (1993) scheme and by information obtained from incubating the sediments in a bio-geochemical microcosm.

2. Materials and methods

2.1. Study area and field sampling

The entire course of the river Trave is located in a landscape, the subsoil of which forms the terminal moraine of the Weichselian glacial period. Its lower reaches nowadays form the entrance to one of the most important German Baltic ports. As in many estuaries, navigability in this area can only be guaranteed by maintenance work. In this context, the river bed of the Trave has been deepened, straightened and shortened through breakthroughs several times in the past centuries. At the same time wide (shore) areas are subject to special protection (e.g. Habitats and Birds Directive).

The German Federal Institute of Hydrology provides an information system of results from physical, chemical, and ecotoxicological investigations of sediments and suspended matter for the German Federal Waterways and Shipping Administration (SedKat). Based on this data set, by means of hierarchical cluster analysis, taking into account the physicochemical parameters fine grain content, TOC, DOC and the contents of As, Pb, Cd, Cr, Cu, Ni, Hg, Zn, S, P and N in bulk sediments and eluates, five characteristic sediment types were identified in the study area: (i) highly compacted marls with low metal and nutrient contents; (ii) a small area with sediments with high contents of N and P in the city Lübeck; (iii) organic silts with lower metal(loid) contents; (iv) organic silts with elevated metal(loid) contents; and (v) sandy sediments of the mouth of the river Trave (refer to Fig. 1).

For this study, four sites were chosen to be investigated (refer to Fig. 1) based on the key parameter organic carbon and contaminants. Three spots represent organic silt sediments with increased metal(loid) contents. The fourth spot represents reworked Pleistocene material (sampling site 3) as it is found in clearly defined areas where the Pleistocene underground protrudes through the recent sediments. It serves as a reference for the geochemical background most pristine with respect to manmade pollution. Information on sediment properties is given in the Supporting Information (SI; section 1.1-1.3).

At all four locations three sediment cores with an inner diameter of 15.5 cm were taken and three dialyses samplers were applied by scuba divers on 05-10-2016 (sampling site 1 and 2) and 10-18-2016 (sampling site 3 and 4). The water depth was between 4.5 and 8 m. After sampling the sediment cores were immediately placed in tanks (PP, Auer Packaging, Germany) filled with surface water sampled at the same location for transportation and storage. In the laboratory, the cores were stored at 10 °C (similar to measured temperatures at the sites) in darkness. The oxygen concentration of the tank water was monitored and maintained close to the values measured at the sampling sites by bubbling air via a glass air stone (JBL, Germany) and a membrane pump (Sera air 110 plus, Germany) when necessary.

2.2. Chemicals and material

Ultrapure water was produced with a USF ELGA Purelab Plus system (ELGA LabWater, Germany). Nitric acid (HNO_3, 65 % w/w, for analysis) was purchased from Merck GmbH (Germany) and re-distilled using a DST-1000 (Savillex, USA).

All samples for inductively coupled plasma-triple-quadrupole mass spectrometry (ICP-QQQ-MS, Agilent 8800 series; Agilent Technologies, Germany) analysis were collected in 15 mL centrifuge tubes (VWR catalyst Laboratory Services, USA, cleaned in 1.3 % nitric acid for > 24 h rinsed with ultrapure water), acidified to a concentration of 1.3 % HNO_3 and stored frozen till measurement.

Prior to acidification aliquots of 0.5 mL of every sample were separated in 1.5 mL microcentrifuge tubes (StarLab, Germany) and stored frozen for ion chromatography measurements (Metrohm 881, Metrohm, Switzerland; Dionex ICS 1100, Thermo Fisher Scientific, USA).

2.3. Ex-situ suction-based pore water sampling

Three profiles of suction-based pore water across the SWI were sampled from each sediment core in the lab using the meso profiling and sampling system (*messy*) (Schroeder et al., 2017). In this process aqueous samples are constantly extracted by a peristaltic pump (REGLO Analog, MS-2/8, ISMATEC, Germany), while a sampling probe is moved across the SWI with a step motor (Motorized Microprofiling, Unisense, Denmark). The synchronization of a fraction collector (Omnicoll, LAMBDA Laboratory Systems, Switzerland) enabled the sampling of defined depth intervals. It is positioned in a glovebox using Argon to prevent re-oxidation of the samples. From 4 cm above sediment surface to 16 cm depth samples were taken with a spatial resolution of 1 cm. Prior to evacuation, samples were filtered with syringe filters (pore size 0.45 µm, Minisart NML Syringe Filters, surfactant-free cellulose acetate, Sartorius, Germany) to obtain the fraction < 0.45 µm.

Profiles of the E_h and the O_2 saturation were measured in parallel to the sampling process with Mansfeldt-type electrodes (ecoTech Umweltmeßsysteme GmbH, Germany) connected to an Ag/AgCl-reference electrode (REF321, Radiometer Analytical, Germany) and a Multi-channel Fiber Optic Oxygen Meter (OXY-3 SMA) equipped with optical oxygen sensors (Oxygen Dipping Probe DP-PSt3) and temperature probes (Pt 100, all PreSens, Germany).

2.4. *In-situ dialyses-based pore water sampling*

In-situ pore water samples were obtained using acrylic modified Hesslein *in-situ* pore water samplers (Rickly Hydrological CO, USA), called pore water peepers, with cavity volumes of 10 ml, equipped with 0.45 µm polyether sulfone membranes (Pall Laboratory, Germany). Prior to use, the acrylic sampling devices and the membranes were cleaned in 1.3 % nitric acid for > 24 h, rinsed with ultrapure water to remove contaminations and subsequently stored in ultrapure water, treated with N_2 for > 14 days to remove dissolved oxygen traces. Two days before deployment the peepers were mounted, with special care being taken to ensure that all cavities were completely filled with ultrapure water. For the transport to the sampling sites the mounted peepers were stored in ultrapure water previously treated with N_2 to limit the diffusion of O_2 in the acrylic parts.

Three peepers per sampling site were deployed for 14 days with a distance of approximately 0.5 m by scuba divers. To protect the membranes the peepers were covered by butyl rubber mats during transfer from aboard the ship to the sediment and back. Samples were extracted from the peepers immediately after their sampling on board ship by perforating the membranes with pipette tips and transfer in acid cleaned 15 ml centrifuge tubes (VWR catalyst Laboratory Services, USA). After removing a 0.5 ml aliquot for IC measurements, samples were immediately acidified for ICP-QQQ-MS measurements (cf. SI paragraph 2).

2.5. *Suspension experiments*

After sampling of pore water was finished 500 g wet weight of a pooled sample from each sediment core and 1 L of natural water (same sampling site as the respective sediment) were fed to a biogeochemical microcosm system (slurry reactor, Mikrokosmossystem MRE2, UIT Umweltleistungen, Germany). It consists of a glass vessel that can be hermetically sealed with an airtight lid equipped with a stirrer to keep the sediment in suspension and electrodes to measure the E_h (EMC 133, Meinsberger Elektroden, Germany) and the pH value (EGA 142, Meinsberger Elektroden, Germany). Data was stored with a logger (MRE2 Datenloggereinheit, UIT Umweltleistungen, Germany). An automatic-valve gas regulation system enables automatic control of the E_h by adding N_2 or O_2 (to lower or increase the E_h, respectively). The sediment was left in suspension untreated to equilibrate at its “natural” E_h. Thereafter, the E_h was forced to -150 mV, 0 mV and 150 mV and kept within E_h windows of approximately 20 mV. At every redox state 2 samples (5 mL) were extracted through a PES porous hollow fiber (Pijpker Laboratorium Technik, Netherlands, 0.45 µm) using a peristaltic pump (Preciflow, LAMBDA Laboratory Systems, Switzerland). The extracted volume was replaced with ultrapure water to keep the sediment/water ratio, resulting in a dilution of < 10 % over the course of the experiment.

2.6. *Sequential extraction*

To create a basic understanding on the release to be expected, the binding forms of the metal(loid)s were examined following a modified BCR scheme (Ure et al., 1993). Even though the fractions of a sequential extraction procedure are necessarily operationally defined, they are considered to represent the amount of an element that is easily exchangeable or carbonate bound (exchangeable), associated with amorphous Fe and Mn oxides (reducible), sulfides and organic material (oxidizable) or the crystalline structures of sedimentary minerals (residual) (Tessier et al., 1979). These fractions were determined in exact 0.5 *g* of freeze dried (Christ Gefriertrocknungsanlagen GmbH, Germany) and milled (planetary mill pulverisette, Fritsch, Germany) subsamples taken at 4 − 5 cm depth from the sediment cores. The exchangeable fraction was extracted with 20 ml 0.11 M acetic acid, the reducible fraction with 0.1 M hydroxylamine hydrochloride. The oxidizable fraction was extracted with ammonium acetate after organic substance removal by repeated addition of hydrogen peroxide. In all cases the extraction included 16 h overhead shaking (ELMI Ltd., Latvia), subsequent centrifugation (20 min, 1700 rpm) and decanting. After each extraction step, the residues were purified by rinsing with ultrapure water and centrifugation. Finally, residual fractions were calculated as the difference between pseudo total content, determined after microwave assisted digestion in reverse *aqua regia* (2,5 mL 30 % HCl + 7,5 mL 65 % HNO_3, refer to SI, section 1.2 for details) and the sum of the three fractions.

2.7. *Analysis*

The metal(loid)s and the nonmetals C, P and S in the pore water, microcosm samples and the sequential extracts were quantified by means of ICP-QQQ-MS. To measure the non-metals simultaneously with the metal(loid)s, the metal(loid)s and nonmetals were calibrated separately. Additionally, a matrix matching was performed by adding NaCl to a concentration of 10‰ to all standards used for calibration and to quality control samples to account for the salinity. Details on the isotopes analyzed and the reference materials used for measurement validation can be found in the SI (Table S5).

To quantify PO_4^{3-}, SO_4^{2-} and NH_4^+ by ion chromatography despite the salt concentration of ∼10 PSU 40 µl of non-acidified samples were diluted 1:50 and standard addition by 0.1 mg/L was applied to exceed the respective limit of quantification.

The anionic species were quantified with a Metrohm 881 compact IC Pro equipped with a Metrosep A Sup 5 Guard 4.0 guard column and a Metrosep A Supp7 separation column (all Metrohm, Switzerland). 3.6 mM sodium carbonate solution was used as eluent and 100 mM sulfuric acid as regenerating acid.

The parallel quantification of the cation NH_4^+ was performed by a Dionex ICS 1100 equipped with an IonPac CG16 − 4 µm RFICTM 4*50 mm guard column and an IonPac CS16 − 4 µm 4*250 mm separation column (all Thermo Fisher Scientific, USA) with 25 mM methyl sulfonic acid as eluent.

2.8. *Statistics and graphs*

Data analyses were performed using R (version 3.3.2; 2016-10-31). Outliers in the measured concentrations and correlation coefficients were identified/calculated using the R packages “outliers” and “PerformanceAnalytics”. Concentrations below the limit of detection (< LoD) were set to half of the respective LoD for statistical calculations. The presented graphs were prepared using Origin 2017 G (OriginLab, USA).

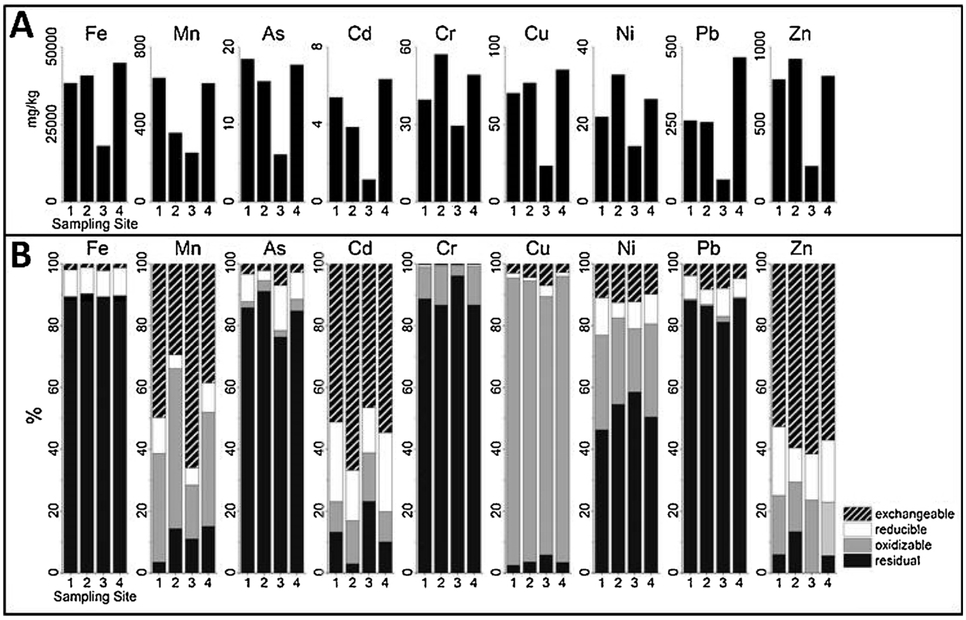

Fig. 2. Total content (A) and binding form (B) of Fe, Mn, As, Cd, Cr, Cu, Ni, Pb and Zn in the sediments of sampling site 1 to 4. Data is presented as average value of the sediments of a sampling site. Corresponding graphs for Ag, Co, Mo, Sb, Se, Sn and V are given in the SI (Fig. S2).

3. Results and discussion

3.1. Metal(loid)s fractionation

Despite differences in total content, the metal(loid)s are partitioned very comparable in the four fractions addressed by the modified BCR scheme in the four sampling sites investigated. Ag, As, Cr, Fe, Mo, Sn, Pb and V remain in the residual fraction to a large extent ($>$ 80 %), Cd, Mn and Zn are available predominantly in the acid-soluble fraction and Ni, Co, Cu, Sb and Se predominantly in the oxidizable fraction (refer to Fig. 2 and SI, Fig. S2). Thus, the metal contaminations of the studied sediments are not reflected in a changed distribution between the binding forms, which contradicts a frequently expressed assumption (Cao et al., 2015; Saleem et al., 2015).

The release of the different geochemical fractions to the environment can be expected if conditions become more acidic (acid-soluble), more reductive (reducible) or more oxic (oxidizable), while the residual fraction is regarded as immobile (Tessier et al., 1979). Thus, the release of the reducible fraction into the pore water of undisturbed sediments with increasing depth is to be expected, while the release of predominantly oxidizable bound elements is likely to occur during sediment resuspension events.

3.2. O_2-concentration and E_h during ex-situ suction-based pore water sampling

The O_2 concentration profiles measured in parallel to *ex-situ* suction-based pore water sampling in the laboratory show that oxygen penetration depth in the sediment cores of sampling sites 1–3 is less than 1 mm. It is slightly larger in the cores from sampling site 4 where the values vary between $<$ 1 mm and up to and up to 3 mm. Additionally, the values confirm that the oxygen concentrations measured during sampling on site (data not shown) were successfully maintained in the laboratory. Profiles of the O_2 concentration are given in the SI (Fig. S3).

The E_h-profiles measured in parallel to *ex-situ* suction-based pore water sampling display a rapid change from oxic ($>$ 100 mV) to anaerobic ($<$ -100 mV) conditions within in the first 2-5 mm below the SWI in the sediment cores of sampling site 1, 2 and 4, while the E_h in the depth profiles of sampling site 3 fluctuates around -100 mV (refer to Fig. 2 and SI, Fig. S4).

3.3. Pore water depth profiles

Results of individual measurements are given in the SI (Tables S11-S143). In both the *in-situ* dialyses-based and the *ex-situ* suction-based samples maximum concentrations measured were in the range of $0.1 - 1$ µg/L for Cd, Sb, Sc and Tl, in the range of $1 - 10$ µg/L for As, Cr, Cu, V, Pb, Mo, Ni, Se, Sn and Ti, in the range of $10 - 100$ µg/L for Zn, in the range of $1 - 10$ mg/L for C and Mn, in the range of $10 - 100$ mg/L for Fe, P, PO_4^{3-} and NH_4^+ and in the range of $100 - 2000$ mg/L for S and SO_4^{2-}.

The concentrations measured in the different *in-situ* dialysis-based pore water depth profiles of the individual sampling sites are very similar. Significantly higher differences were found repeating the *ex-situ* suction-based pore water depth profiles of the individual sampling sites. This effect can be ascribed in non-homogenized “living sediments” to the visible macro-biota and bioturbation activity and the resulting sediment heterogeneities (Teal et al., 2013; Stockdale et al., 2009). Whereas the temporal and spatial “smoothing” over exposure time ($\sim$14 days) and cavity width (up to 10 cm) of the *in-situ* dialyses based pore water sampling explains the lower variation of the these profiles. However, comparing averaged pore water depth profiles obtained with the two completely different sampling techniques as shown in Figs. 3 and 4, results remain remarkably comparable for most of the analytes. Taking into account the different sampling principles (passive *vs.* active) and the capability of *messy* to make sediment heterogeneities visible, it seems possible to generate sediment pore water samples in the laboratory that represent field conditions. This is especially from interest when not scuba diver, but only sediment corer based sampling is possible due to, e.g. economic reasons or water depth.

Next to profiles of the E_h the dissolved concentrations of C, P and PO_4^{3-}, NH_4^+, S and SO_4^{2-}, Fe and Mn in *ex-situ* suction-based and *in-situ* dialyses-based pore water depth profiles are shown in Fig. 3. In the pore water depth profiles of all sediments the concentrations of C, P, PO_4^{3-} and NH_4^+ increase with depth, while the concentrations of dissolved S and SO_4^{2-} decrease. The concentrations of dissolved Fe and Mn experience pronounced peaks below SWI with Fe concentrations being the most variable between the individual *ex-situ* suction-based depth profiles of all analytes in the mg/L range. Also the averaged depth profiles obtained for Fe *in-situ* show larger variations than most other analytes.

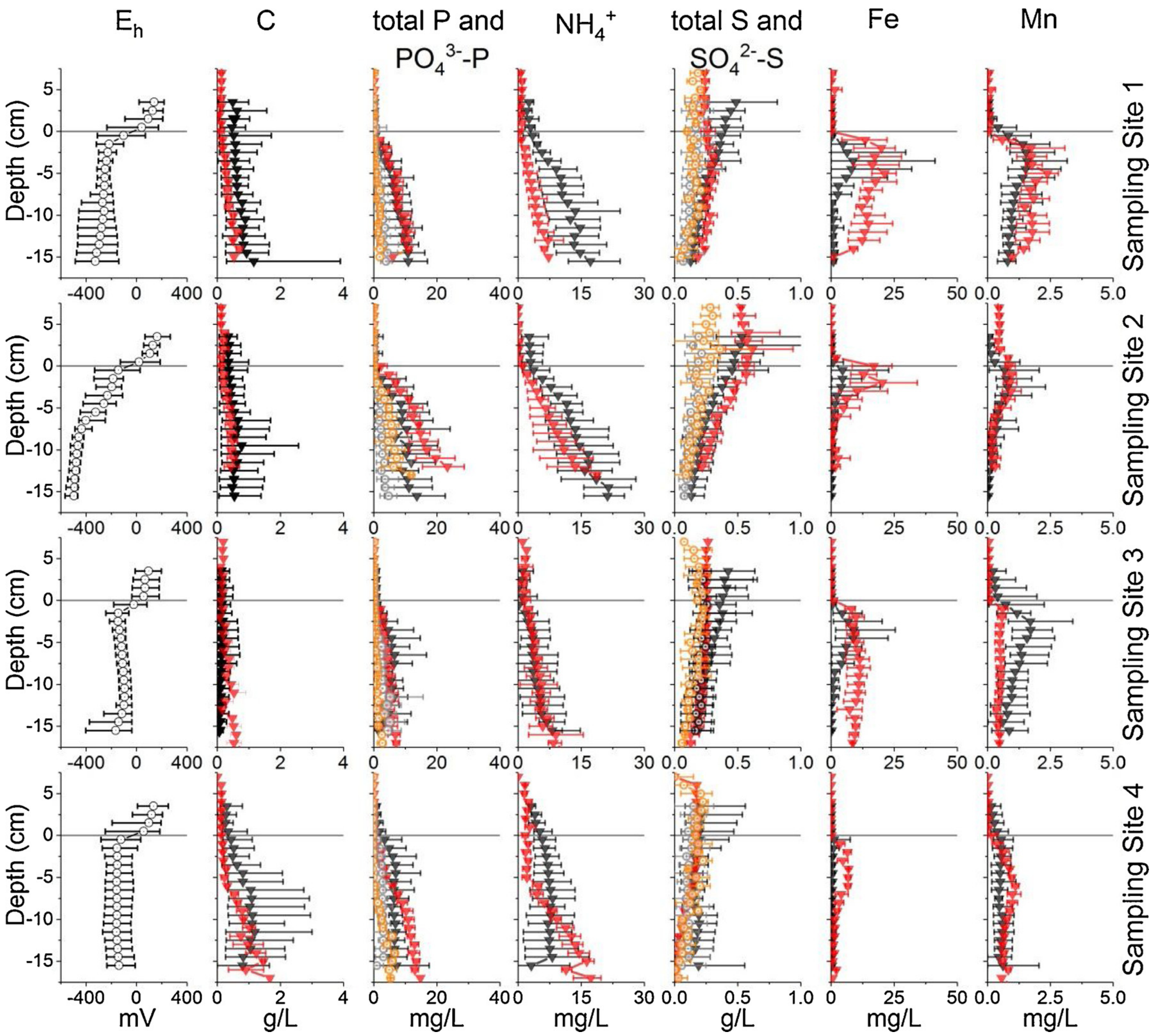

Fig. 3. E_h (○) and laterally averaged dissolved concentrations of C, total P, NH_4^+, total S, Fe and Mn in *ex-situ* suction-based (n = 9, black) and *in-situ* dialyses-based (n = 3, red) pore water samples at the four sampling sites. With total P and total S also PO_4^{3-}-P and SO_4^{2-}-S are given in the *ex-situ* suction based (grey) and *in-situ* dialyses based (orange) samples. Error bars represent the minimum and maximum value / concentration measured at the respective depth. Grey lines represent the SWI (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

The release of NH_4^+ and PO_4^{3-} can be attributed to a large extent to organic matter (OM) decomposition. Accordingly, significantly higher concentrations of both analytes are reached in the organic-rich sediments of sampling sites 1, 2 and 4 than in the reworked Pleistocene material of sampling site 3. On the other hand a relevant difference between total dissolved P and dissolved PO_4^{3-}-P that increases with increasing concentrations of dissolved C in this organic-rich sediments indicates that the amount of dissolved organic matter (DOM) increases with depth. Since for H_2S no analytical method was available, the total S concentrations determined by ICP-QQQ-MS represent essentially SO_4^{2-}-S. This is confirmed by the good agreement between total-S concentrations and SO_4^{2-}-S concentrations determined by IC. However, S is also incorporated in DOM (Ksionzek et al., 2016) explaining the total S concentrations being slightly above the SO_4^{2-}-S concentrations.

The depth profiles of Fe and Mn are in good agreement with the measured redox profiles and reflect the rapid transition from oxic to anaerobic conditions in organic-rich sediments. The release of both elements by reductive dissolution of their (hydr)oxides as well as Fe and Mn precipitation by the formation of sulfides with increasing sulfate reduction are well studied diagenetic processes. (Du Laing et al., 2009)

Pore water depth profiles of the trace metal(loid)s As, Cd, Cr, Cu, Ni, Pb and Zn are shown in Fig. 4. Corresponding graphs for Ag, Co, Mo, Sb, Se, Sn and V are given in the SI (Fig. S5). The concentrations of the metal(loid)s were either approximately constant from the water column to maximum sampling depth (Ag, Pb, Zn), decreased to values near the respective limit of detection within the first centimeters below the SWI (Cu, Mo, Ni, Sb) or increased with depth (Cr, Se, Sn, V). Pronounced concentration peaks below the SWI characterize the depth profiles of As, Cd, and Co. In addition, their concentrations show the greatest variability in the first 3 − 4 cm below the SWI both, in *ex-situ* suction-based and *in-situ* dialyses-based samples. Hence, with respect to the similarities to major elements grouping of the metal(loid)s addressed in this study based on the shape of their pore water depth profiles in Fe/ Mn-type (As, Cd, Co, Zn), C/P/ NH_4^+-type (Cr, Se, Sn, V) and S-type (Cu, Mo, Sb) appears appropriate and reflects important processes controlling their solubility. The essential control of Fe and Mn (hydroxides) on the mobility of As and Co, as shown in the Trave sediments, has been described before (Mitsunobu et al., 2006; Dang et al., 2015; Heggie and Lewis, 1984; Stockdale et al., 2010; Gorny et al., 2015). However, their reductive dissolution contributes to increased concentrations only in the uppermost 2 − 3 cm of the sediments. With depth increasing concentrations of the elements Cr, Se, Sn and V indicate their release during OM degradation. The decreasing concentrations and limited availability in the pore water of Cd, Cu, Mo, Ni and Sb are explainable by their affinity for sorption to binding sites of particulate OM or caused by sulfide precipitation (Huerta-Diaz and

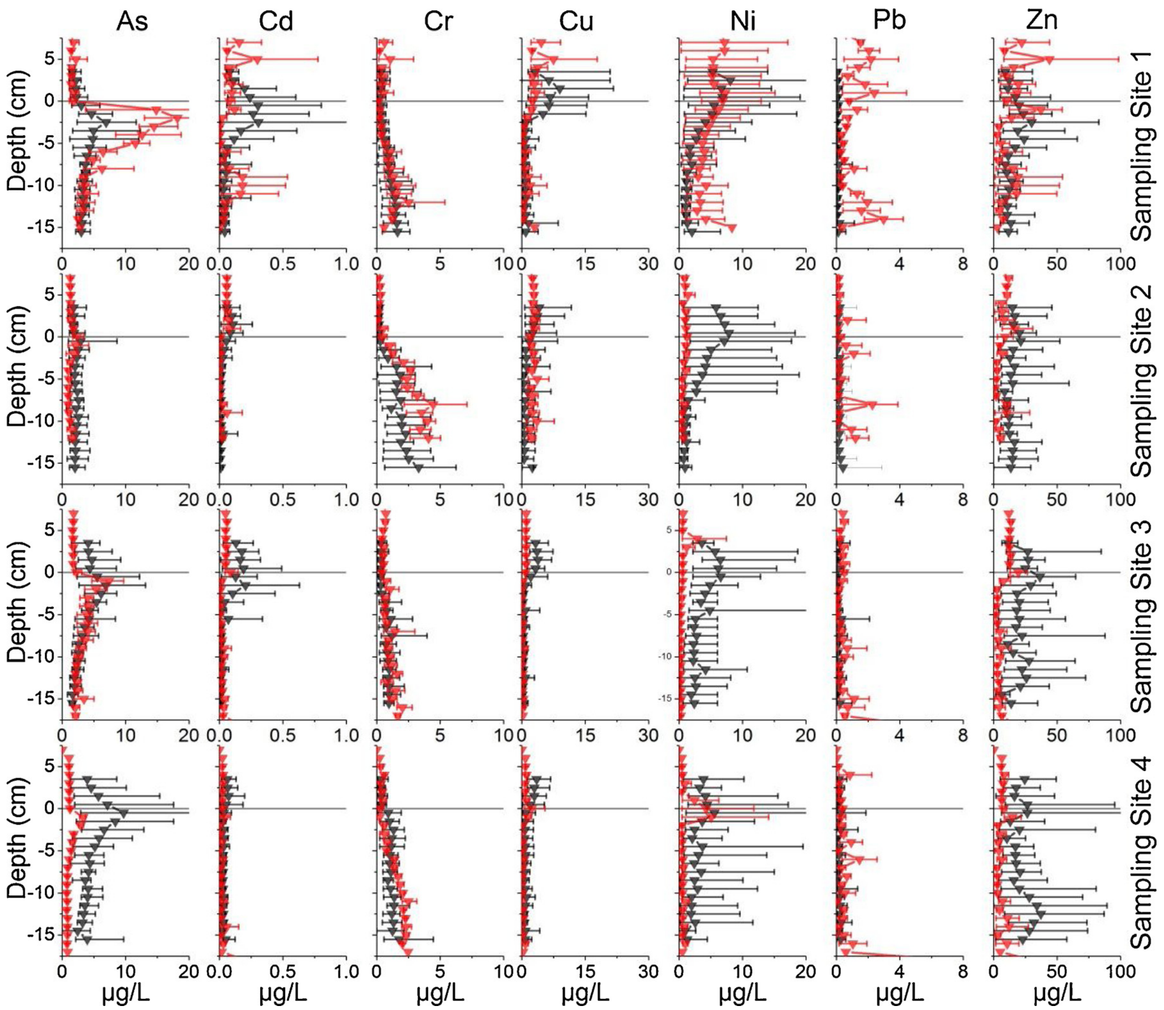

Fig. 4. Laterally averaged dissolved concentrations of As, Cd, Cr, Cu, Ni, Pb and Zn in *ex-situ* suction-based (n = 9, black) and *in-situ* dialyses-based (n = 3, red) pore water samples at the four sampling sites. Error bars represent the minimum and maximum value/concentration measured at the respective depth. Grey lines represent the SWI (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

Morse, 1992; Morse, 1994; Morse and Luther, 1999). Based on the elements which were present in significant proportions (> 5%) in the reducible fraction of sequential extraction (As, Cd, Co, Sb V, Zn), only V was continuously or increasingly released into the pore water with increasing depth.

3.4. Suspension experiments

The measured concentrations of S, Fe, As, Cd, Ni and Pb are shown in Fig. 5 as a function of E_h. Corresponding graphs for C, P, Mn, Ag, Co, Cr, Cu, Mo, Sb, Se, Sn, V, Zn and changes of E_h and pH value during the individual experiments are given in the SI (Fig. S6-S7). The “natural” E_h that occurred in the sediment suspensions before the E_h was forced to defined values of -150 mV, 0 mV and +150 mV reached mostly values between -100 mV and -300 mV. The pH value and E_h are two interdependent measures in the way that an increase in E_h leads to a decrease in pH as consequence of H + ion formation during oxidation and vice versa (Yu et al., 2007). Corresponding changes in pH also occurred during the redox manipulations in the mesocosm. However, all measured pH values were between 7.5 and 9.5.

Regarding the metal(loid)s, maximum concentrations across all experiments were < 1 µg/L for Cr, Sc, Sn, Ti and Tl, 1 − 10 µg/L for Ag, Cd, Cu, Pb, Sb and Se, 10 − 100 µg/L for As, Co, Ni and V and 100 − 1000 µg/L for Mo and Zn. Maximum concentrations of Fe and Mn were about 50 and 6 mg/L respectively. An increase in concentrations in the liquid phase < 0.45 µm with increasing E_h can be found for S and the metal(loid)s Cd, Co, Cu, Ni, Sb and Zn with largest amounts of all 6 metal(loid)s being released from the reworked Pleistocene material of sampling site 3. In addition, the increase in release starts at lower E_h values than in the organic-rich sediments of the other sampling sites. A similar redox behavior of these elements was observed in comparable experiments with different soils and sediments by several authors (Shaheen et al., 2016, 2014; Frohne et al., 2011, 2014). The reason for the increased metal(loid) release with rising E_h can be the oxidative dissolution of sulfide minerals (Morse, 1994; Schippers, 2004) while the constant C and P concentrations in the course of the experiment indicate that aerobic degradation of OM was of minor importance (Gerringa, 1990). On the other hand, the increase in metal(loid) concentrations is limited by their re-sorption on existing surfaces and the co-precipitation with Fe and Mn (hydr)oxides (Calmano et al., 1993) leading to significant alteration of metal(loid) binding forms during resuspension (Xie et al., 2019).

The increasing release of Cd, Co, Cu, Ni, Sb and Zn with increasing E_h agrees well with the results of the sequential extraction where all these elements were found in the oxidizable fraction in significant proportions (> 10 %) in all four sediments. However, only small proportions of the oxidizable bound fraction were released to the aqueous phase. The proportion of the metalloids Cr and Mo in the oxidizable fraction was as well more than 10 % without being released at increasing E_h. The latter may be caused by the affinity of both elements to

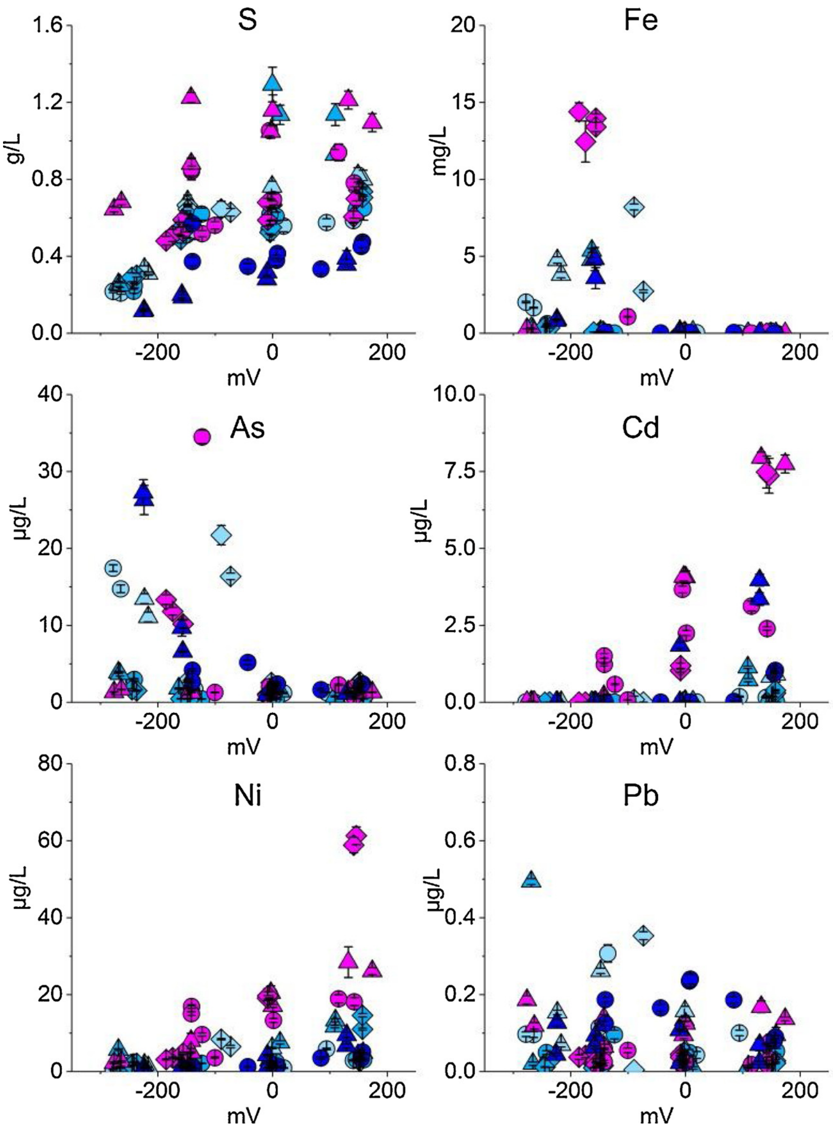

Fig. 5. Concentrations of S, Fe, As, Cd, Ni and Pb as a function of E_h (●, ●, ●, ● for sampling site 1, 2, 3 and 4; ●, ▲, ◆ representing the different sediment cores). Error bars represent analytical standard deviation (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

OM or by the lower solubility of their oxidized species (Cr(VI), Mo(VI)) compared to their reduced species (Cr(III), Mo(IV)) (Gorny et al., 2016; Smedley and Kinniburgh, 2017).

3.5. Data evaluation with respect to dredging and reuse

Results of sequential extraction are frequently evaluated by application of concepts such as enrichment factor (EF) (Abrahim and Parker, 2008), geoaccumulation index (Igeo) (Iqbal and Shah, 2011), individual or global contamination factor (ICF or GCF) (Zhao et al., 2012) and risk assessment code (RAC) (Jain, 2004). The application of EF and Igeo (refer to SI, section 7) indicate that next to Cd, Pb and Zn, that exceed the German threshold values for dredged material, also As, Ag, Se and Sn are severely enriched in the sediment samples of sampling site 1, 2 and 4 (refer to SI, Table S7). Application of the ICF and RAC (refer to SI, section 7) predicts the highest risk of release into the aqueous environment for Cd and Zn or Cd, Cu, Sb and Zn, respectively. The risk of release for all elements is estimated to be the lowest for sediments of sampling site 3.

Assessment of dissolved concentrations can be conducted by comparison with predicted no effect concentrations or other (eco-)toxicity measures (Mayer et al., 2014). However, such values delivering sufficient reliability are not available for all elements addressed in this study. Stricter threshold values for the dissolved concentrations of more elements (As, Cd, Cr, Cu, Fe, Ni, Pb, Sb, Se, Zn) than in other regulations are specified in the European Drinking Water Directive (EC, 1998). Regarding the pore water of the undisturbed sediments these values, developed for human consumption not ecological issues, delivering here a very conservative reference value, are only exceeded by Fe and As in some of the near-surface samples. Assessment criteria for dissolved metal mixtures in sediment pore water taking into account the metals Cd, Cu, Pb, Ni and Zn were developed by USEPA (refer to SI, section 8) (U.S. EPA (2005)). In the *ex-situ* suction-based pore water samples the assessment criteria is exceeded by most of the samples of the first 1 – 2 cm below SWI, by individual samples from all four sampling sites and in each case almost a complete depth profile of the locations 2 and 4 (refer to SI, Table S9). This delivers an indication that sediment dwelling organisms are exposed to elevated metal(loid) concentrations. Although this underlines the heterogeneity of the sediment surfaces, it does not reveal any higher toxicity of the contaminated sediments compared to the sediment treated as background reference.

With regard to the suspension experiments, the metal(loid)s released per dry mass of sediment can be calculated. The maximum amounts released per kg sediment are computed to be < 0.1 μmol for Ag, Cr, Se, Sn, and Pb, between 0.1 and 1 μmol for Cd, Cu and Sb, 1 – 10 μmol for As, Co, Mo, Ni and V and approximately 50, 450 and 3500 μmol for Zn, Mn and Fe, respectively. This corresponds to a maximum expected release of the order of 10^{-1} % of the average daily load from river Trave (calculated from data of the surface water monitoring of the federal state Schleswig-Holstein in the years 2005–2014; data not shown) per ton sediment suspended for Cd, 10^{-2} % for As, Ni and Zn, 10^{-3} % for Cu and PO_4^{3-} and 10^{-4} % for Cr and Pb.

This indicates that a singular, time-limited resuspension event significantly affects the budget of only few analytes, compared to the continuous load of the Trave, even if quantities typically relocated during a single dredging campaign are considered.

However, the European Water Framework Directive specifies maximum permissible concentrations for dissolved Cd, Ni and Pb (0.45–1.5 depending on water hardness, 34 and 14 μg/L, respectively). These values are exceeded for Cd and Ni in the sediment suspensions by up to ~16 and ~2 times, respectively. This suggests that, depending on the hydrological conditions, a spatial and temporal impairment of water quality is to be expected in case of dumping of the examined sediments as dredged material. However, the expected impairment is largest for the most “pristine” sediment of sampling site 3, initially treated as reference.

4. Conclusions

During dredging the investigated sediments, the dissolved metal (loid) fractions of the sediment pore waters contribute only to a minor extent to the water column content, while this release path may be crucial for NH_4^+. From the results of the resuspension experiments and the application of RAC to the sequential extraction findings, a risk of release for the elements Cd, Cu, Sb and Zn can be derived. On the other hand, application of the RAC did not predict the observed release of Ni and Co, and the lower predicted risk for sampling site 3 did not match the observations of the resuspension experiment.

The results suggest that despite the visible enrichment, from anthropogenic causes, for most of the sediments studied, only minor metal (loid) release must be expected, which is in good agreement with observations during monitoring of dredging operations (de Groote et al., 1998; Pieters et al., 2002; Morgan et al., 2012). Nevertheless, metal (loid)s and nutrients are among the key substances when it comes to improvement of the ecological state of the Baltic Sea (HELCOM, 2010) and next to their release into the water phase bio-methylation, ingestion or dermal uptake cause environmentally harmful effects. However, the results emphasis once again, that dredged sediments have to be seen as a potential secondary resource in, e.g. recreation efforts. Therefore, miss matching evaluation criteria, neglecting the onsite fractionation and speciation of the potentially hazardous substances may cause a significant loss of management opportunities and may bear in themselves the risk to create ecologically unnecessary cost increases.

CRediT authorship contribution statement

Henning Schroeder: Investigation, Data curation, Visualization, Writing - original draft. **Lars Duester:** Conceptualization, Methodology, Data curation, Writing - review & editing. **Anne-Lena Fabricius:** Methodology, Investigation. **Dennis Ecker:** Methodology, Investigation. **Vera Breitung:** Conceptualization, Project administration, Writing - review & editing. **Thomas A. Ternes:** Supervision, Writing - review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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Appendix A. Supplementary data

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