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SEDIMENTS, SEC 1 • SEDIMENT QUALITY AND IMPACT ASSESSMENT • RESEARCH ARTICLE

Reactivity and potential mobility of metals in human-impacted harbor sediments (Port of Rotterdam, the Netherlands)

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Abstract

Purpose Vast amounts of harbor sediments are being dredged every year globally. These sediments are often enriched in potentially toxic elements (PTEs), the abundance and potential mobility of which are important for sustainable harbor management practices. In this study, we investigate metal (especially PTE) distribution, abundance, and reactivity in sediments along a salinity gradient in the waterways of Europe's largest harbor, the Port of Rotterdam.

Materials and methods Bulk surface sediments were analyzed for general physicochemical properties (e.g. grain size, total metal concentration). From selected locations covering the local salinity gradient, sediments were subjected to three independent chemical extractions to determine chemically reactive metal pools. Additionally, metal retention in two contrasting sediments (high versus low salinity) was further explored using pH-dependent leaching experiments in combination with a geochemical model.

Results and discussion The majority of the investigated sediments consisted predominantly of silt and were rich in organic matter. Concentrations of Cd, Pb, Zn, Cu decreased with increasing salinity. Concentrations of Al, Fe, V correlated negatively with grain size, because these geogenic metals are enriched in fine-grained silicates. Results from the chemical metal extractions showed clear differences in the reactivity and mobility potential of metals, that could be grouped into four clusters. The combined chemical and modeling results indicate that sorption onto metal (oxyhydr)oxides and organic matter as well as precipitation of metal sulfides and carbonates control metal retention. High reactivity and mobility potential were observed for Pb, Cd, Zn, particularly at low pH. Limited spatial variability in metal chemistry along the salinity gradient indicates that the highly variable depositional conditions have little impact on metal behaviors.

Conclusions Chemical extractions and pH-dependent leaching experiments revealed distinguishing metal reactivities from four clusters. Our results provide insight into metal distribution in the dynamic estuarine environment of the Port of Rotterdam and highlight the importance of understanding chemical speciation in addition to abundance for harbor sediment management.

Keywords Harbor sediment · Chemical extraction · Metal mobility · pH-dependent leaching

1 Introduction

Harbor dredging to maintain or deepen waterways generates large quantities of sediments worldwide annually (Mymrin et al. 2017). Europe alone produces over 300 million m^3 per year (Crocetti et al. 2022). Dredged harbor sediments are variable mixtures of water, minerals, and organic matter (OM), often containing a wide variety of pollutants. Evaluating the impact of perturbing such sediments for instance by dredging and relocation and, nowadays, the feasibility of potential reuse in an ecosystem context (Vermaat et al. 2005) requires information on physical and chemical sediment properties, particularly the potentially toxic metals

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or elements (PTEs). Assessing the risk of PTEs requires, beyond quantification of the total metal concentrations (Rodrigues et al. 2010), insight into the chemical forms in which metals are present, which controls PTE reactivity and potential mobility (Couvidat et al. 2017).

The reactivity of metals (particularly PTEs) depends on the proportion of the total metal concentration that is biogeochemically reactive (Römkens et al. 2009; Miranda et al. 2021). The reactive metal fraction is available for interaction with the dissolved phase, on short time scales of less than seconds up to days, through processes such as sorption/desorption and (surface) precipitation/dissolution reactions (Groenenberg et al. 2017). The extent of these interactions (which can mobilize metals) depends on metal speciation. For instance, metals precipitated as carbonates, bound to metal (oxyhydr)oxides or OM are relatively labile pools that can be (re)mobilized when environmental conditions (redox, pH) change. By contrast, metals sequestered in silicates represent a relatively recalcitrant pool from which metal release is limited (Rodrigues et al. 2010). Sediment dredging and relocation introduces changes in environmental conditions (e.g. pH, redox, salinity) that can affect metal mobility and fate, the extent of which can be estimated with insight into the chemical distribution of PTE in the sediments.

Wet chemical extractions are commonly used to investigate metal retention mechanisms and estimate overall metal reactivity in sediments. Single-step extractions for determining the reactive metal fraction involve strong complexing agents (e.g. ethylenediaminetetraacetic acid (EDTA) or dilute acids (e.g. HCl, HNO_3) with various concentrations, reacting durations and temperatures (Rodrigues et al. 2010; Cappuyns 2012; Brady et al. 2016; Gil-Díaz et al. 2019). Many studies used 1 M HCl (1–24 h) to extract reactive metals from marine and estuarine sediments (Burton et al. 2006; Larner et al. 2008; Choi et al. 2012; Leleyter et al. 2012; Morgan et al. 2012; Gil-Díaz et al. 2019). These extractions can release metals associated with carbonates, acid-volatile sulfides (AVS), poorly crystalline Fe/Mn (oxyhydr)oxides, and from surface sorption sites of OM and clay minerals (Claff et al. 2010; Morgan et al. 2012; Job et al. 2020). Another widely applied extraction method uses dilute HNO_3 to determine reactive metal concentration in both soils and sediments (Dijkstra et al. 2004; Römkens et al. 2009; Groenenberg et al. 2017; Sakan et al. 2021; Gao et al. 2022). Groenenberg et al. (2017) reported 0.43 M HNO_3 extraction recovered more than 90% of reactive metals predicted by a geochemical model. The procedure standardized as ISO 17586:2016 using 0.43 M HNO_3 has therefore been proposed in the Dutch regulatory framework to assess the potential environmentally available metals in soils and soil-like materials (ISO/TC 190 2016; Vink et al. 2017). Although 1 M HCl and 0.43 M HNO_3 extractions are relatively fast and cheap to estimate reactive metal concentrations in both soil and sediments, they are not intended to provide information on chemical forms of metals.

To distinguish different pools of metals in sediment, sequential wet chemical extractions are based on the successive exposure of a solid sample to extractant solutions of increasing strength and/or of different characteristics (Burton et al. 2006; Kraal et al. 2013; Zhang et al. 2014). Typically, sequential extraction protocols can differentiate between metals from highly reactive fractions such as exchangeable and pH-sensitive pools to less reactive fractions such as crystalline (oxyhydr)oxides and OM-bound metals. Although these metal pools are operationally defined and thus do not provide direct information on metal species, they may offer insights into metal pools and retention relevant to metal reactivity and potential mobility (Zimmerman and Weindorf 2010; Vollprecht et al. 2020).

In addition to chemical metal fractionation, the actual mobilization of reactive metals (i.e. transfer from the solid to the liquid phase) is of prime environmental concern because it affects surface water and groundwater quality. The metal mobilization process is strongly influenced by pH of the surrounding environment (Król et al. 2020). The pH levels influence solubility of (heavy) metal carbonates, sulfides and labile (oxyhydr)oxides. Additionally, an important part of reactive (heavy) metals are associated with solid phase through adsorption on minerals (e.g. clay, Fe/Al (oxyhydr)oxides) or organic surfaces with a pH-dependent charge (Patricia et al. 2006; van der Sloot et al. 2007; Groenenberg and Lofts 2014; Król et al. 2020) and hence also pH-dependent desorption. This results in a general increase in metal leaching with decreasing pH, where dissolved metal concentrations can vary orders of magnitude in response to environmentally relevant pH changes (Dijkstra et al. 2004). Geochemical multi-surface models, considering metal adsorption to various soil constituents (i.e. organic matter, (oxyhydr)oxides, clay minerals), have successfully predicted solid-solution partitioning and speciation of PTEs in soils with a wide range of physiochemical properties (Dijkstra et al. 2009; Groenenberg and Lofts 2014; Gao et al. 2022). Hence, combined detailed chemical metal fractionation, pH-dependent leaching behavior and chemical modeling may provide a valuable toolbox with which to assess metal retention, reactivity and mobility in soils and sediments.

To assess the potential meal leaching as a consequence of dredging, we investigated relationships between depositional conditions, sediment properties and detailed metal distribution in sediments with different salinities. Sediments from the Port of Rotterdam (PoR), one of the world's major ports and an area of intense (chemical) industrial activity

are deposited under a salinity gradient from the seaside to the inland, resulting in contrasting environmental conditions that temporally vary as a result of tidal change. We compared two commonly used single-step extractions (1 M HCl and 0.43 M HNO_3) for estimating the fraction of reactive metals, with a six-step sequential extraction for metal fractionation. We performed pH-dependent leaching experiments to obtain a better understanding of metal retention and specifically sorption processes, and thereby provide insight into potential metal mobilization processes under oxidation-acidification scenario's associated with sediment disturbance. We modeled the solid-liquid partitioning of reactive metals as a function of pH using a mechanistic multi-surface adsorption model. Outcome of the experiments and the modeling is potentially of importance in policy making for sediment management practices and environmental risk assessment.

2 Materials and methods

2.1 Study area and sample collection

The Port of Rotterdam is located in the Rhine-Maas estuary in Zuid-Holland. Every year, dredging activities in the PoR yield 12–15 million m^3 of dredged materials with chemical properties that result from the mixed marine and terrestrial origin, with an important impact (contamination) from human activities (Kirichek et al. 2018). Sediments are mostly extracted via hopper dredgers and transported to coastal disposal sites in the North Sea or, in case of contaminated sediment, to a confined facility for submerged long-time storage. In the summer of 2021, a sampling campaign was conducted in the PoR waterways during which sediment was sampled at 49 locations throughout the harbor (Fig. 1). Sediments down to ~50 cm sediment depth were collected using a gravity corer. On deck, the content of the corer was emptied into 2-L polypropylene buckets that were closed, stored at 4 °C and transported to Royal Netherlands Institute for Sea Research (NIOZ) within a few days. Here, porewater was immediately extracted and sub-samples for chemical analyses were taken and stored frozen. All 49 sediment samples were subjected to total elemental composition analysis in porewater and solid phase. Sediments from 13 locations (red in Fig. 1), different in salinity and contamination levels (Kirichek et al. 2018), were selected from the riverine–marine continuum and further applied for three independent chemical extraction procedures. Two sediments from site 115 and site 21 A, where the major amounts of marine and riverine sediments being dredged respectively (Kirichek et al. 2018), were also used in the humic substances extraction and the pH-dependent leaching experiment.

2.2 Porewater analysis

Bulk sediments were thoroughly homogenized with a spatula in the buckets. Approximately 40 mL of wet sediment were transferred into 50 mL polypropylene centrifugal tubes (Falcon) and centrifuged at 3000 rpm for 20 min (HERMLE Z 446). In a N_2-purged glove bag, the porewater was immediately filtered using 0.45-µm nylon syringe filters (MDI) and sub-sampled for various analysis (Table 1). Due to the limited porewater volume, salinity was estimated based on porewater sodium concentration relative to the average seawater sodium concentration of seawater with a salinity of 35 (Steele et al. 2010; IJsseldijk et al. 2015).

2.3 Solid phase analysis

The sediment residues after centrifugation were stored at −20 ºC under N_2 prior to further analysis. Before homogenizing and subsampling, the sediment residues were left in a N_2-purged glove bag overnight to thaw. One subsample

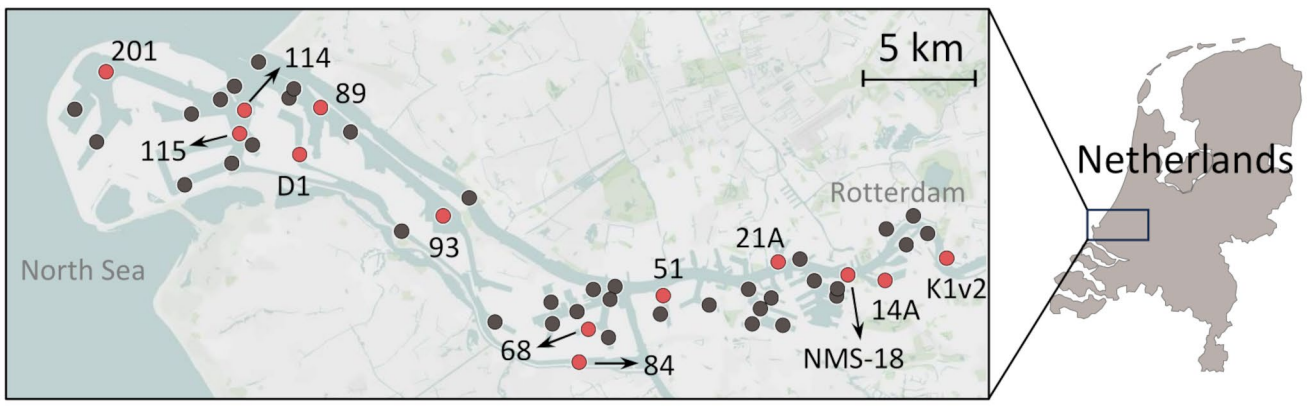

Fig. 1 Sampling locations in waterways of the Port of Rotterdam, the Netherlands. Red dots indicate key sites covering the land-to-sea (riverine-to-marine) transition; these sediments were used for detailed chemical metal analysis in addition to bulk sediment properties

Table 1 Porewater pre-treatment and analysis. Porewater metal measurement included Al, as, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, V, Zn, na

Analyte	Pre-treatment	Storage (ºC)	Measurement
NO_3^-, NO_2^-, NH_4^+	None	−20 ºC	Continuous flow analyzer (TRAACS 800+)
HPO_4^{2-}, Si	Acidified to pH ~ 1 with 4 M suprapur HCl	4 ºC	Continuous flow analyzer (TRAACS 800+)
DIC	Diluted 10× in degassed 25 g L^{-1} NaCl	4 ºC	Continuous flow analyzer (QUAATOR)
Metals	Diluted 30–900× in 1 M double distilled HNO_3	4 ºC	HR-ICP-MS (Thermo Scientific, Element 2)

Table 2 The three chemical extractions used in this study. F1–F6 refers to the sequential extraction, and the calculated residual fraction (total minus sum of steps F1–F6) is denoted as F7. F3, F4, F5 were modified from Tessier et al. (1979) to accommodate for the data requirement in geochemical modeling

Fraction	Extraction	Target phase	Term	Reference
F1	1 M $MgCl_2$ (1 h)	Exchangeable	$MgCl_2$	(Tessier et al. 1979)
F2	1 M Na-acetate/acetic acid, pH 4.5 (50 ºC, 5 h)	Bound to pH-sensitive pool (i.e. carbonates, acid volatile sulfides)	ACE	(Tessier et al. 1979)
F3	50 g L^{-1} Na_3-citrate/50 g L^{-1} $NaHCO_3$/20 g L^{-1} ascorbic acid, pH 8 (24 h)	Bound to poorly ordered, easily reducible oxides	ASC	(Tessier et al. 1979; ISO/TC 190 2012a)
F4	0.35 M acetic acid/0.2 M Na_3-citrate/50 g L^{-1} Na-dithionite, pH 4.8 (60 ºC, 4 h)	Bound to reducible oxides	DITH	(ISO/TC 190 2012b)
F5	0.2 M NH_4-oxalate/0.2 M oxalic acid, pH 3 (4 h)	Bound to crystalline oxides	OXA	(ISO TC/190 2012c)
F6	Concentrated HNO_3 (60 ºC, 6 h)	Bound to OM, pyrite	HNO_3	(Keon et al. 2001)
F7	-	Residue	Residue	-
-	1 M HCl (24 h)	Reactive metals	RM HCl	(Morgan et al. 2012)
-	0.43 M HNO_3 (2 h)	Reactive metals	RM HNO_3	(ISO/TC 190 2016)

of wet sediment residue (~ 1 g) was added to 50 mL of 3 g L^{-1} sodium pyrophosphate solution, followed by gently hand shaking for particle disaggregation. The bulk grain size distribution was measured by the Coulter laser particle sizer (Beckman Coulter), from which percentages of clay (0–2 µm), silt (2–63 µm), sand (63–2000 µm) and D50 (i.e. median grain size) were obtained. Another subsample of wet sediment residue (~ 10 g) was freeze-dried (Hetosicc freeze drier) for 72 h and manually ground with agate pestle and mortar. The freeze-dried sediments were further subsampled for various analyses.

One freeze-dried sub-sample (~ 10 mg) was used for total carbon (TC) analysis by a CN element analyzer (Thermo Scientific, FLASH 2000). To determine total organic carbon (TOC), a separate sub-sample (~ 0.5 g) was decalcified with 1 M HCl and subsequently analyzed by the CN analyzer. For TC and TOC analysis, sediments from 115 to 21 A were analyzed in triplicate, which showed a relative standard deviation (RSD) < 10%. To quantify the adsorption surface of OM for two contrasting sediments used in pH-dependent leaching experiment (Sect. 2.4 and 2.5), separate sub-samples of the freeze-dried sediments (~ 2.5 g) from site 115 and 21 A were subjected to the rapid batch procedure for humic acid (HA) and fulvic acid (FA) extraction according to van Zomeren and Comans (2007). The extracted HA and FA in form as dissolved organic carbon (DOC) were measured by a carbon analyzer (Shimadzu).

To determine the total concentrations of metals of interest in sediment (i.e. Al, As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, V, Zn), a thoroughly ground sub-sample (~ 0.1 g) of freeze-dried sediment was subjected to total digestion (2.5:1:1.5:1 concentrated HF/HNO_3/$HClO_4$/HCl, details in supplementary information). The digest was diluted with in-house, sub-boiled double-distilled 1 M HNO_3 prior to element analysis by HR-ICP-MS (Thermo Scientific, Element 2). Triplicates were included for four samples in total digestion. The RSD was < 5% between the triplicates for all here reported elements. A marine sediment reference material (MESS-3, National Research Council of Canada) was digested and analyzed in triplicate. The recoveries were 90–100% for all elements (except 85% for V) with RSD's from 4 to 7%.

Freeze-dried sub-samples (~ 0.25 g) of thoroughly ground sediment from 13 selected sites (indicated in red in Fig. 1) were transferred into sets of three 15 mL Falcon tubes for three independent chemical extractions (Table 2): a sequential extraction modified from Tessier et al. (1979), 1 M HCl extraction (24 h) (Morgan et al. 2012), and 0.43 M HNO_3 extraction (2 h) (Groenenberg et al. 2017). For each extraction step a volume of 10 mL of extraction solution was used. Samples were centrifuged at 3000 rpm for 20 min following each extraction step. The supernatant was filtered through 0.45-µm nylon filters, except for the concentrated HNO_3 step at the end of the sequential extraction. From these samples, 0.1 mL of the supernatant was pipetted into 4.1 mL 1 M HNO_3. The 'residual' (refractory, non-reactive) metal fraction (F7; Table 2) was calculated as the difference between metal concentration from total digest and the sum of fractions 1 to 6 of the Tessier sequential extraction. The sum of F1–6 can be considered 'reactive' in the sense that

these metals can react in the sedimentary environment on timescales of seconds to hundreds or thousands of years (Canfield et al. 1992; Poulton and Canfield 2005). As such, reactivity here extends beyond the timescales of short-term reactivity and mobility probed by single-step HNO_3 and HCl extractions – metal pools extracted by the latter two extractions are referred to as highly reactive. The elements of interest in the mixtures were analyzed by HR-ICP-MS. Sediment from station 115 was included in triplicate in the 0.43 M HNO_3 extraction and 1 M HCl extraction, with RSD < 5% for all elements (except Mo, which showed an RSD of 11%). Extractions were performed at room temperature (20 ºC) if not specified; extractions at elevated temperature were performed in a water bath with thermostat. All chemicals used were of analytical grade or higher. To test the effect of sample treatment (freeze-drying, grinding) on metal distributions, untreated sub-samples of the anoxically thawed wet sediment were included in the extraction procedures.

2.4 pH-dependent Batch leaching experiments

Sub-samples of the freeze-dried and ground sediments from two locations with contrasting porewater salinity (115 as marine, and 21 A as riverine) were used in a pH-dependent leaching experiment aimed to determine pH-sensitivity of metals to provide insight into the mechanisms involved in metal retention versus availability. Approximately 3 g of sediment were subjected to batch leaching for 48 h in 50-mL Falcon tube at various pH levels ranging from 2 to 10 adjusted by manually adding 0.1 – 5 M HNO_3 or NaOH (EMSURE ACS, Reag.). The sediment was kept in suspension by shaking horizontally on a shaking table (Edmund Bühler SM30) at 125 rpm. At 0 h, 0.5 h, 2 h, 4 h, and 44 h, the tubes were briefly opened for pH measurement using a ROSS pH electrode (Thermo Fisher Scientific) and, if necessary, readjusted to the target value with small additions of 0.1 – 5 M HNO_3 or NaOH. After 48 h, the experiments were terminated. Equilibrium was assumed to be achieved as the pH changes between 44 h and 48 h were less than 0.3. Suspensions were filtered using 0.45-µm nylon syringe filters, followed by liquid analysis detailed as in Sect. 2.2 and 2.3, including measurement of Al, Ba, Ca, Fe, K, Mg, Mn, Na, SO_4, Si, Sr, Cd, Pb, Ni, Cu, Zn, Cr, V, As, Co, PO_4, DIC, and DOC in the leachates.

2.5 Multi-surface sorption modeling

A multi-surface sorption model (Dijkstra et al. 2004) constructed in the ORCHESTRA software (Meeussen 2003) was used to explore metal speciation and subsequently pH-dependent leaching behaviors of seven PTEs (Cr^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Cd^{2+}, Pb^{2+}, Zn^{2+}) in sediment from two contrasting locations: 115 (marine) and 21 A (riverine). The geochemical model considered: specific and/or non-specific sorption processes onto particulate (SOM) and dissolved (DOM) organic matter based on the NICA-Donnan model (Kinniburgh et al. 1999); sorption to Fe/Al (oxyhydr)oxides based on the generalized two-layer model (GTLM) (Dzombak and Morel 1991; Meima and Comans 1998); sorption to clay minerals based on Donnan model (Kinniburgh et al. 1999). The ASC-extractabel Fe (oxyhydr)oxides and the OXA-extractable Al (oxyhydr)oxides (for methodological details, see Table 2) were both assumed to have a specific surface area of 600 m^2/g (Dzombak and Morel 1991), while the DITH-extractable Fe (oxyhydr)oxides were assumed to have a specific surface area of 100 m^2/g (Hiemstra et al. 1989). Both SOM and DOM were represented by HA in the model with the assumption that HA consists of 50% carbon. The reactive SOM was derived from total reactive OM (i.e. HA/FA extraction, see Table S4) and reactive DOM in the leachates (i.e. total reactive OM = HA + FA = reactive SOM + reactive DOM). The detailed model description is elaborated in Dijkstra et al. (2004). The default values of sorption parameters were used in the model, while the required input data (Table S4) such as reactive surface concentrations and reactive metal concentrations were obtained from sediment analyses and the pH-dependent leaching experiments.

2.6 Data analysis

Data analysis was conducted in RStudio. Hierarchical clustering analysis (R packages: 'cluster', 'factoextra') was used to group metals with similar chemical fractionation patterns. The optimal number of clusters was determined by k-mean approach (Elbow method). A principal component analysis (PCA) was performed to study the relationship between sediment metal contents and other geochemical properties. Input data was normalized prior to PCA analysis. The analysis was performed in RStudio with the package 'FactoMineR'.

3 Results

3.1 General characteristics of sediments and deposition environment

The salinity measured in the pore-waters from the investigated sediments ranged from 0.7 in the eastern, river-dominated area to 30.5 in the western, marine-dominated area (Fig. 2). At most stations (42 out of 49), sediments were silt-rich (silt fraction > 60%) with D50 < 25 µm (Table 3).

Based on salinity and D50, depositional settings were classified into six categories, of which the mean values of key parameters are presented in Table 3. In silt-rich sediments, TOC values ranged from 9.0 to 1.7%, showing a decreasing trend with increasing salinity ($R^2 = 0.69$, Fig. 2). The small subset of more sand-rich sediments (D50 > 50, sand fraction > 45%) showed relatively low TOC (0.4–2.0%) that was negatively correlated with D50 ($R^2 = 0.55$, Fig. 2).

The concentrations of metals showed strong spatial variability. Metal concentrations were higher in silt-rich sediments compared to sand-rich sediments (Table 3). This applied to both Dutch regulated PTEs (As, Cd, Co, Cr, Cu, Mo, Ni, Pb, V, Zn) and non-regulated metals (Al, Fe, Mn). Specifically, most PTEs showed similar distributions patterns as TOC: highest concentrations occurred in silt-rich, low-salinity sediments (e.g. 2.15 ± 0.66 mg kg^{-1} for Cd) and lowest concentrations in sand-rich, high-salinity sediments (e.g. 0.18 mg kg^{-1} for Cd). Compared to the average concentrations of PTEs in Dutch marine clay deposits (later referred as 'background concentration'; Mol et al. 2012), enrichment (defined as the ratio of PTE concentration to background concentration) was observed for most investigated PTEs in silt-rich sediments (Fig. S1 a), with the greatest enrichment (i.e. 4–10 times the background concentrations) observed for Cd, Cu, and Zn in the silt-rich, low salinity sediments. However, despite this enrichment, PTE concentrations in both sediments and porewaters mostly remained below the Dutch sediment intervention values (Fig. S1b, Table S2) and groundwater intervention values (Table S3).

3.2 Chemical metal fractionation

In contrast to total metal concentrations, chemical fractionation showed similar patterns for the individual metals across PoR depositional environments (Fig. 3 for selected metals; remaining measured metals are shown in Supplementary Information, Fig. S2). High variability in leaching behavior between individual metals rather than between depositional environments was also reflected in hierarchical clustering analysis: the total within-cluster sum-of-squares was relatively low between depositional (location) clusters (Fig. S3) compared to metal clusters (Fig. 4). Additionally, we observed sediment pre-treatment (i.e. freeze-drying and grinding) had limited impact on metal chemical fractionation (Fig. S4). Compared to anoxic wet pristine sediments, pre-treated sediments showed higher recovery rate and more homogeneity. Thus, our interpretation is based on the freeze-dried ground samples.

For the four metal clusters, we present the chemical fractionation results for representative PTEs (Cr, Ni, Cu, Pb) from each cluster (Fig. 3). Cluster 1 (Al, Cr, V) showed a dominant residual (refractory, unreactive) fraction generally > 0.6, for Al even > 0.8. Metals in Cluster 2 (Fe, Ni, Co, As) showed relatively low reactivity as reflected by a relatively large, combined pool (0.5–0.8) of residual and concentrated HNO_3-extractable (poorly reactive) metals. Cluster 3 metals (Cu, Mo) occurred predominantly in a form that was extracted by strong reducing agents (so likely associated with crystalline metal (oxyhydr)oxides), but also showed a large exchangeable ($MgCl_2$-extractable) fraction

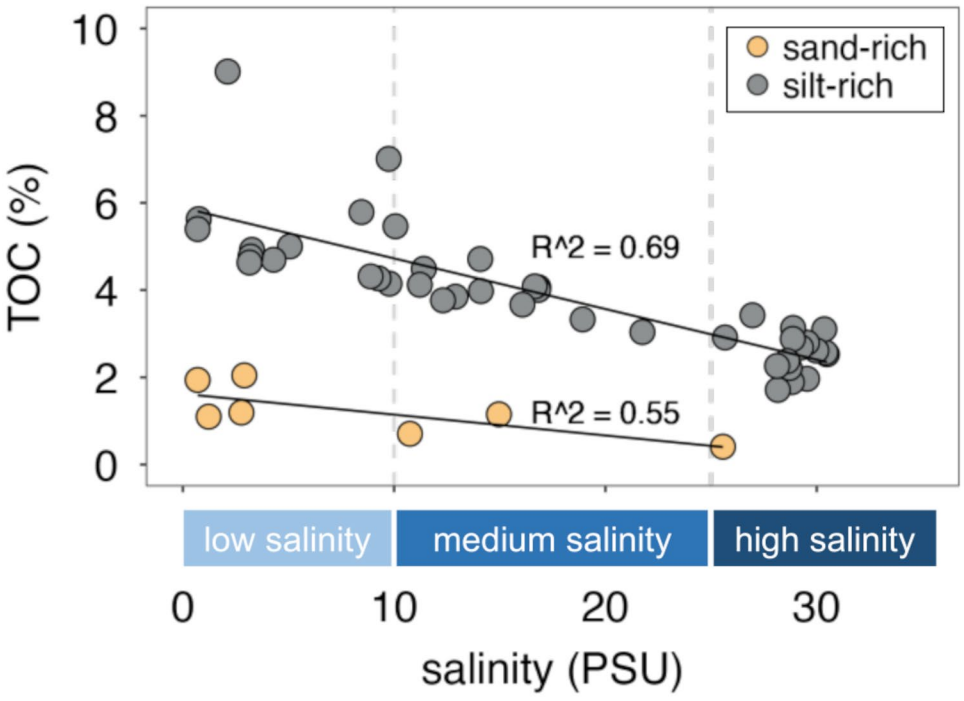

Fig. 2 TOC content of 49 sediment samples taken throughout the PoR area. Sediments were classified into low salinity (0–10), medium salinity (10–25), high salinity (25–35), and silt-rich (> 60% silt, D50 < 22 µm) versus sand-rich (> 45% sand, D50 > 54 µm). The trendlines with R^2 represent the linear regression relationships of TOC with salinity (p-value < 0.001 for silt-rich sediments; p-value = 0.057 for sand-rich sediments)

Table 3 Mean values with standard deviations of key parameters and metal contents from six depositional settings. Full datasets for individual sites are provided in the supplementary information (table S2, S3)

	Silt-rich ($n=42$)			Sand-rich ($n=7$)		
	High salinity ($n=16$)	Medium salinity ($n=13$)	Low salinity ($n=13$)	High salinity ($n=1$)	Medium salinity ($n=2$)	Low salinity ($n=4$)
salinity	28.9 ± 1.3	14.9 ± 3.4	5.3 ± 3.5	25.6	12.9 ± 3	1.9 ± 1.1
clay fraction (%)	9 ± 2	8 ± 1	7 ± 2	7	4 ± 1	5 ± 1
silt fraction (%)	78 ± 6	79 ± 3	76 ± 5	35	31 ± 5	38 ± 9
sand fraction (%)	12 ± 5	13 ± 3	17 ± 5	58	65 ± 6	57 ± 10
D50 (µm)	12 ± 2	13 ± 1	15 ± 3	113	121 ± 42	106 ± 41
TIC (wt%)	2.6 ± 0.5	2.4 ± 0.4	1.8 ± 0.7	1.5	1.6 ± 0.2	1.4 ± 0.4
TOC (wt%)	2.6 ± 0.5	4 ± 0.6	5.4 ± 1.3	0.4	0.9 ± 0.3	1.6 ± 0.5
Al (g kg^{-1})	47.6 ± 6	57.8 ± 3	57.3 ± 6.6	17.6	26.5 ± 1.5	28.4 ± 1.8
Fe (g kg^{-1})	28 ± 4	35 ± 2	35 ± 4	8	11 ± 2	14 ± 4
Mn (g kg^{-1})	0.6 ± 0.1	1.2 ± 0.16	1.24 ± 0.49	0.17	0.38 ± 0.11	0.43 ± 0.12
As (mg kg^{-1})	17 ± 2	21 ± 3	21 ± 2	6	7 ± 1	10 ± 4
Cd (mg kg^{-1})	0.52 ± 0.13	1.81 ± 1.14	2.15 ± 0.66	0.18	0.33 ± 0.16	0.7 ± 0.31
Co (mg kg^{-1})	9 ± 1.2	13.3 ± 0.9	14.5 ± 1.9	3.2	4.8 ± 0.9	6.5 ± 1.3
Cr (mg kg^{-1})	78 ± 12	114 ± 22	129 ± 41	33	36 ± 8	99 ± 99
Cu (mg kg^{-1})	30 ± 8	71 ± 22	97 ± 28	6	13 ± 5	27 ± 11
Mo (mg kg^{-1})	1.29 ± 0.31	1.3 ± 0.29	1.63 ± 0.72	0.35	0.34 ± 0.01	0.51 ± 0.27
Ni (mg kg^{-1})	29 ± 4	44 ± 8	48 ± 7	9	13 ± 2	19 ± 3
Pb (mg kg^{-1})	48 ± 9	100 ± 28	132 ± 44	17	24 ± 5	68 ± 42
V (mg kg^{-1})	85 ± 15	94 ± 8	86 ± 13	22	26 ± 6	27 ± 3
Zn (mg kg^{-1})	164 ± 38	404 ± 118	550 ± 145	45	88 ± 34	244 ± 176

(0.05–0.25) compared to Cluster 1 and 2. Cluster 4 metals (Pb, Mn, Cd, Zn) were present mostly in the pH-sensitive pool that was extracted at acetate/acetic acid-buffered pH 4.5.

The sequential extraction results provided chemical context to interpret the results from the single-step 1 M HCl and 0.43 M HNO_3 extractions. For Cluster 4, the most reactive metals, we observed good agreement between highly reactive and reactive metal fractions as determined by single-step and sequential extraction, respectively (Fig. 5). For the other clusters, with larger fractions of more stable, less reactive metal pools, we observed an increasing discrepancy between highly reactive (dilute HNO_3 or HCl) and reactive (F1–F6 of sequential scheme). The notable exception to this trend was Mo, which was only limitedly soluble in either 1 M HCl or 0.43 HNO_3. The 1 M HCl (24 h) extraction generally dissolved a larger proportion of the total sediment metal pool compared to 0.43 M HNO_3 (2 h).

3.3 pH-dependent leaching: experimental and modeling results

In the pH leaching experiment and the associated modeling, we continued our focus on four PTEs (Cr, Ni, Cu, Pb; the remaining PTEs in Fig. S5) representing four determined clusters. In general, good agreement in trends was observed between the pH leaching results and the model results, as shown in Fig. 6. Both the experiment and model showed highest fractions of leached metals at low pH (< 4), minimum metal release at circumneutral pH, and slightly enhanced metal solubility at high pH. Although slightly elevated metal concentrations were observed at higher pH compared to circumneutral pH, the released fraction at pH 10 accounted for less than 5% of total metal contents. The results of the multi-surface sorption modeling indicated that metals were predominantly adsorbed metal (Al, Fe) (oxy-hydr)oxides with, for some metals such as Cd and Cu, a significant SOM-complexed fraction (Fig. S7).

Furthermore, the leaching trends were similar for the marine (115) and riverine (21 A) sediment. Sediment from the riverine location showed slightly elevated leached concentrations over the entire pH range, while sediment from the marine location exhibited larger leached metal fractions (except Ni). This observation aligned well with their metal extraction results, where slightly larger reactive fractions of Cd, Pb, Zn and Cu were found in sediment from the marine location.

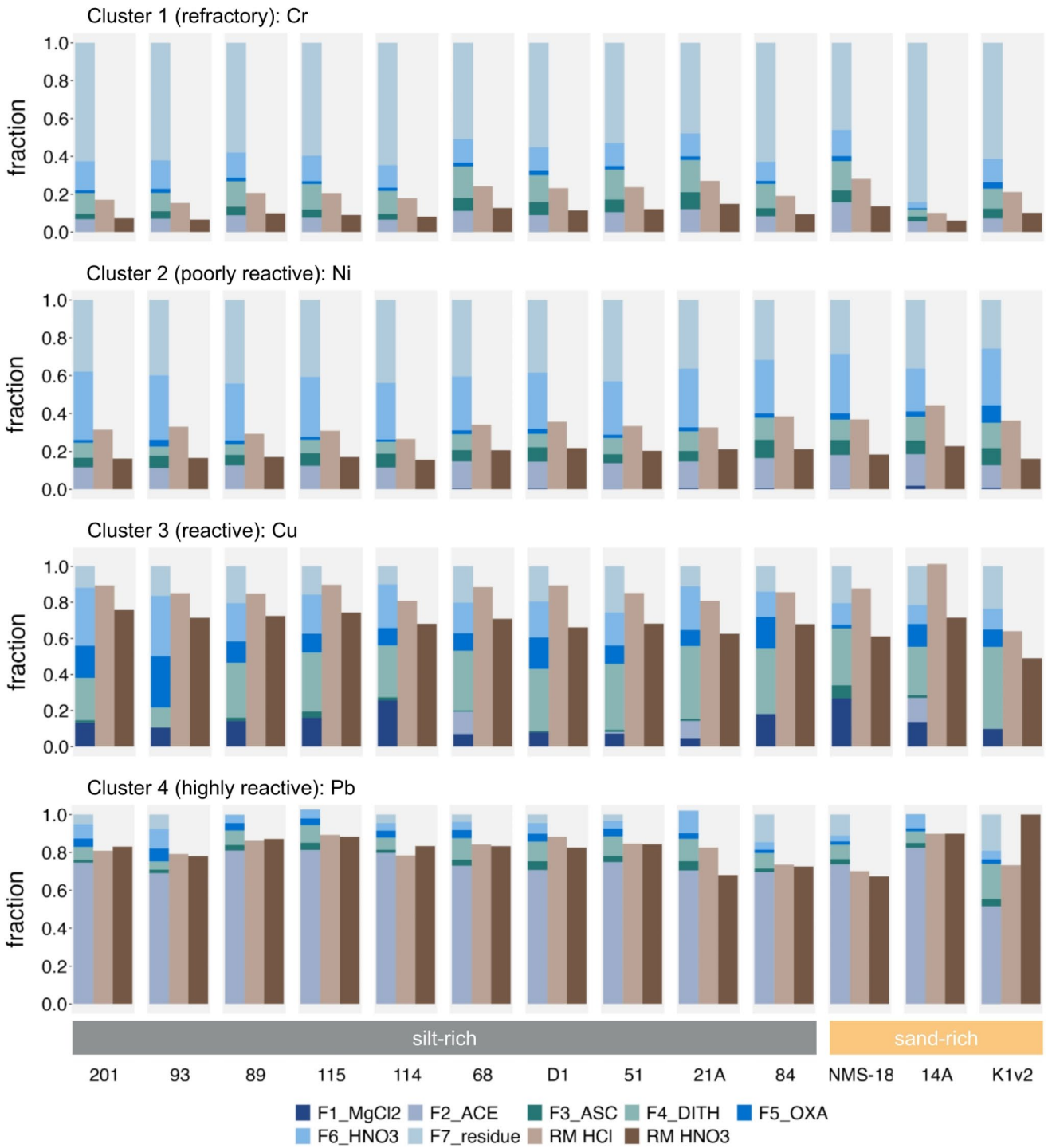

Fig. 3 Chemical fractionations of Al, Fe, Cu, Mo, Pb in the PoR sediments based on three chemical extraction methods

4 Discussion

4.1 Spatial distribution of metals in the PoR

While our results indicate large differences in reactivity between metals, total metal abundance is commonly used to assess sediment quality and potential environmental impact. The investigated PTEs, some (e.g. Cd, Cu, Zn) despite being substantially enriched compared to their background concentrations (4–10 times the average concentrations in Dutch marine clay deposits), were mostly below the Dutch intervention values (Fig. S1b, Table S2) due to the continuous

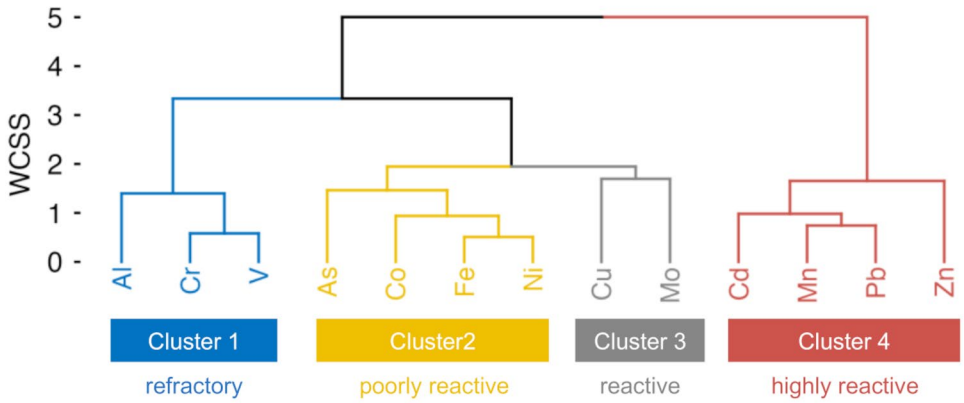

Fig. 4 Hierarchical clustering analysis using Ward's method (minimum-variance method): dendrogram of chemical fractionation based on 13 metals. The total within-cluster sum of squares (WCSS) indicates the statistical dissimilarity between clusters. The number of clusters was determined from k-means approach (Elbow method)

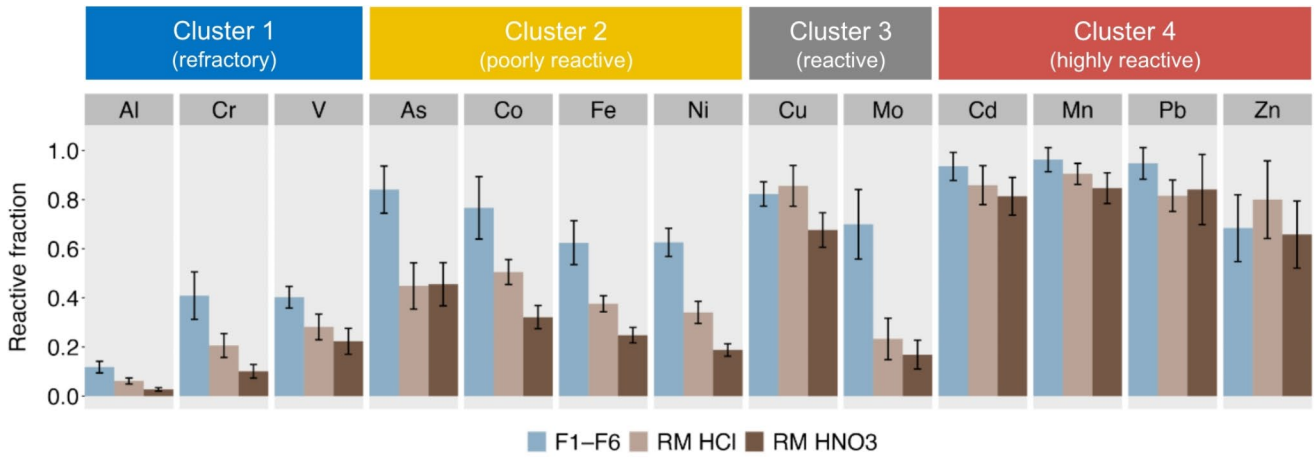

Fig. 5 Extractable fractions by three extraction methods for metals in four clusters. The mean values and standard deviations were calculated from13 sediment samples

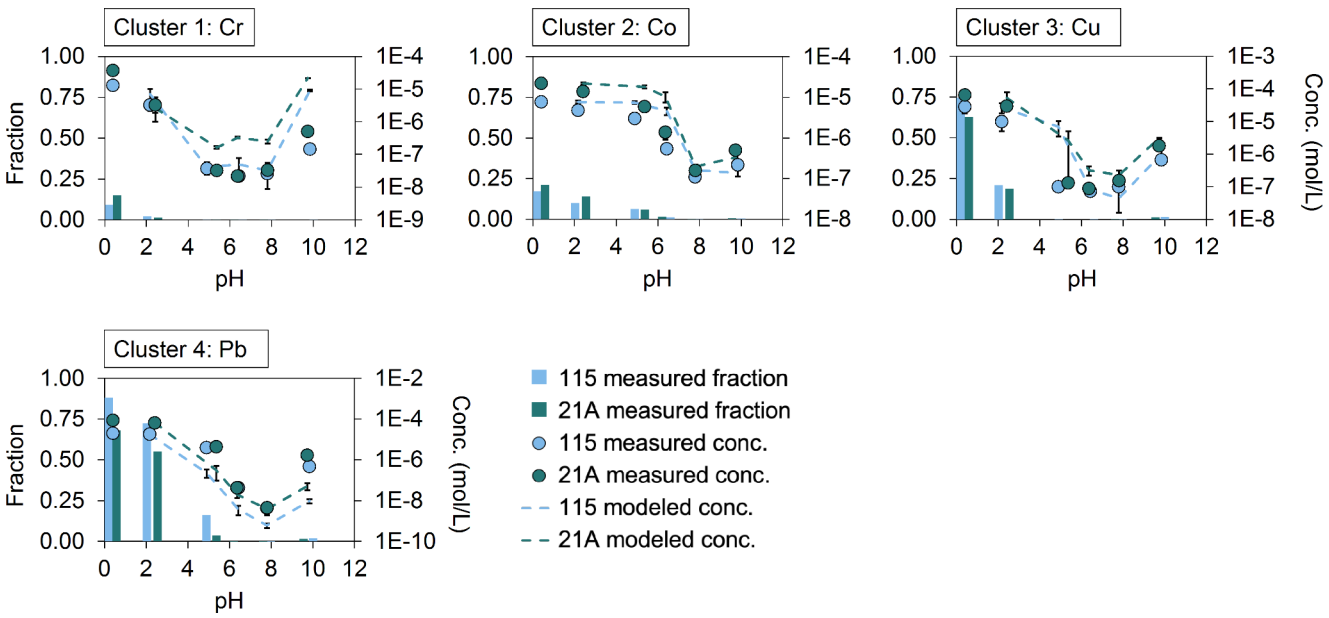

Fig. 6 Measured (circles) and modeled (dashed lines) concentrations of Cr, Ni, Cu, and Pb released from sediment into solution as function of pH, for two contrasting sediments (115 as marine, 21 A as riverine). Leached metals were also expressed as fractions (bars) of the total metal concentration. Primary (left) y-axis and secondary (right) y-axis stand for fraction and concentration. Also included are leaching results for 0.43 M HNO_3 single-step extraction (pH 0.4)

improvement of sediment quality in the PoR over the past decades (Salomons 2005). Currently, more than 90% of the dredged sediment in the PoR is classified as 'clean' (i.e. contaminants, including PTEs, below intervention values), and the amount of contaminated sediment is expected to further decline (Kirichek et al. 2018). Here, we use spatial differences in the distribution of a broad spectrum of metals to unravel key factor controlling metal occurrences and speciation in our study area: anthropogenic and natural inputs, transport, and metal immobilization processes such as adsorption, precipitation, and complexation.

Our results show that concentrations of anthropogenic PTEs such as Cd, Cr, Cu, Pb, Zn in the PoR waterways are higher in fine-grained sediment compared to coarse, sandy sediment (Fig. 7, S2). In addition, these metals are more strongly enriched in the low-salinity (river-dominated) part of the harbor, where values exceed concentrations found in 'average' marine deposits (Fig. 7, S2). This pattern of heavy metal enrichment firstly reflects their predominant terrestrial, anthropogenic source (e.g. traffic, transport, sewage, agricultural runoff; Vos and Janssen 2008), which is strongest in the eastern, river-dominated PoR area. Normalization to Al is not explaining the observed trend. Additionally, the metal retention capacity of clays and silts and the associated organic matter (TOC strongly correlates with these metals; Fig. 7) is much greater than that of marine sand, resulting in enrichment in finer sediment. Metals in coastal aquatic systems can be concentrated at the interface between fresh and salt water due to flocculation and settling processes (Biggs 1970; Jilbert et al. 2018). Additionally, elevated salinity levels have been shown to have adverse effect on the enrichment of heavy metal due to the competitive effect of major cations (e.g. Na, Ca, K) for sorption sites on sediment particles (Du Laing et al. 2008). Despite highly dynamic hydrological conditions in estuaries due to tidal effects, there is limited exchange of sediment between the river-dominated and marine-dominated estuarine realms, maintaining metal distribution patterns (Dyer 1995; Salomons 2005; McLachlan et al. 2017).

The geogenic metals Al, Fe, and V are enriched in the silt-rich sediments compared to sand-rich sediments but without a strong effect of salinity (Fig. 7, S2). The abundance of these metals depends on their deposition associated with fine-grained sediment (rich in silicate minerals containing Al, Fe, V) in relatively low-energy parts of the river-dominated PoR estuarine area.

Some of investigated metals (As, Co, Mn, Mo, Ni) plotted between the geogenic and anthropogenic metals in PCA (Fig. 7). This may result from the interaction of various factors such as diverse sources and precipitation processes. For example, Ni can be of anthropogenic origin but also occurs in clay minerals such as serpentines, chlorites, and smectites (van der Veer 2006; Griffioen et al. 2016). Furthermore, for redox-active metals such as Mn, primary distribution patterns may be altered by (re)mobilization and precipitation processes resulting from complex (repetitive) redox successions in dynamic aquatic environments where bottom sediments can be resuspended (Aller 1998).

4.2 Metal fractionation and reactivity

Although the total metal concentrations in most of the dredged sediments, further relocated to the North Sea (Kirichek et al. 2018), were below the Dutch intervention levels, substantial enrichment of PTEs (particularly Cd, Cu, and Zn) was observed in many samples throughout the harbor (Fig. S1a). This highlights the need for a deeper understanding of metal reactivity when reuse and valorize

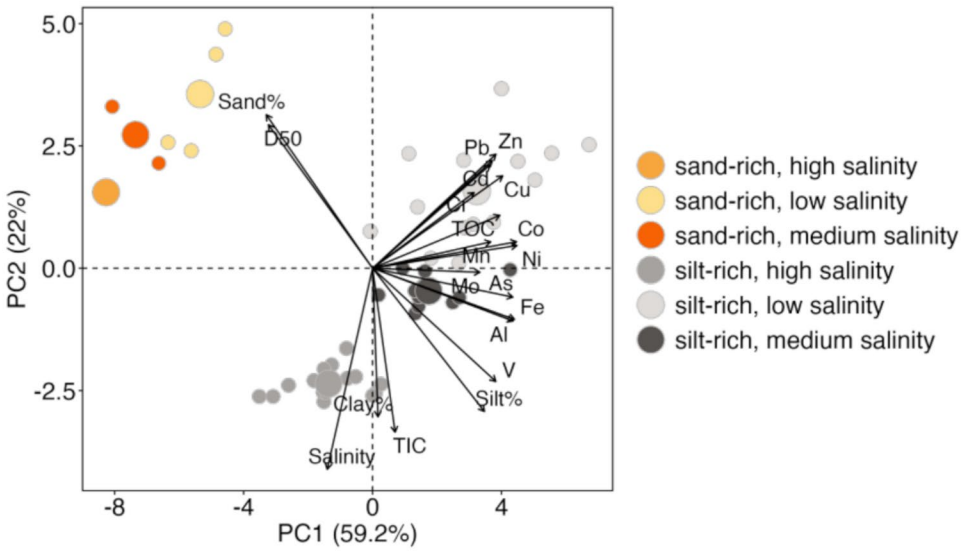

Fig. 7 Principal components analysis (PCA) of key parameters and total metal contents of 49 sediment samples. PC1 and PC2 explained 59.2% and 22% of the total variance, respectively

dredged sediment as construction or agriculture materials. While the total concentration of metals is used to evaluate sediment quality (Brand et al. 2009), potential mobility and environmental concerns are a function of the chemical forms in which metals exist in soils and sediments. Here, we use extensive chemical characterizations of a wide range of (hazardous) metals to show large variability in reactivity and mobility between metals. Below, we evaluate the reactivity of PTEs and the broader metal clusters (as determined here by hierarchical clustering) to which they belong.

Chromium is, depending on its redox state, a potentially hazardous metal (Murthy et al. 2022), but in the PoR sediment shows very low mobility as it is part of the cluster of geogenic metals that likely occur in silicate minerals (Cluster 1; Al, Cr, V; Fig. 5). These metals showed very limited extractability in all extraction schemes (Figs. 3 and 5) and did not dissolve at any pH of the pH leaching experiment (Fig. 6). Given the recalcitrant nature of silicate minerals, these metals are presumed to exhibit high stability and limited sensitivity to (abrupt) changing environmental conditions such as introduced by dredging activities (oxidation and acidification).

The PTEs As, Co and Ni were part of a metal cluster (2; Fig. 5) that showed higher reactive fractions than Cluster 1 (Figs. 3 and 5). For this cluster, we observed relatively large differences between the three extraction methods to determine the reactive metal fraction, with increasing fractions dissolved with increasing strength of the extraction method. Half of the reactive fraction should be considered highly reactive, the other half is less reactive, likely because these metals occurred in association with relatively stable phases such as pyrite and OM (Fig. 3) that are not dissolved in dilute HCl or HNO_3. The relatively low reactivity was further illustrated by limited dissolution during the pH leaching experiment (< 25%; highest at low pH; Fig. 6). Here, we note that Co was the only metal in this cluster that was leached at pH 4–5 (~ 10%; Fig. S5), indicating it was relatively pH-sensitive. These metals are expected to be stable under reducing conditions; sequential extraction indicates that major pools are sulfides, OM and silicates. Long-term exposure to oxidizing conditions, however, likely result in degradation of OM and oxidative pyrite dissolution, resulting in release of these metals. Still we hereby note that formation of metal oxides under such conditions can serve as secondary sink for heavy metals (Zhang et al. 2014; Hu et al. 2022).

Copper formed a metal cluster (3; Fig. 5) with Mo that was distinct from Cluster 2 because of a higher fraction associated with Fe/Al (oxyhydr)oxides (Fig. 3). Additionally, Cluster 3 showed a relatively large exchangeable fraction, which likely reflects the more loosely sorbed part of the Fe/Al (oxyhydr)oxide-associated metal pool (Anderson and Delaney 2000; Kraal et al. 2015). The single-step extractions showed much higher release of Cu than Mo (Fig. 5). The pH leaching experiment further showed that at slightly higher pH (2), Cu solubility was limited (< 20%; Fig. 6) while Mo was not released into solution. Limited extractability of Mo by dilute HCl or HNO_3 was also reported in FeS-rich sediments by Morgan et al. (2012) and in various types of Dutch and Portuguese soils by Groenenberg et al. (2017). The observation that Mo is solubilized by reducing agents (ascorbic acid, dithionite) but not dilute acids suggests that Mo in its anionic form is present as molybdate (MoO_4^{2-}) which remains adsorbed onto positively charged Fe/Al (oxyhydr)oxides that persist at low pH. At high pH, desorption under increasing OH^- concentrations can result in release of these oxyanions, explaining the increased dissolved concentrations of As, Mo and V at high pH (Fig. S5). This pH-dependent mobility is the opposite of that observed for metals that exist as cations in solution such as Cu, Ni and Zn (Król et al. 2020). Dissolved Cu did show a relatively strong increase at high pH (10) in the leaching experiment (Fig. 6), even though the mobilized fraction was very small (< 5%). This increased solubility of Cu (and other heavy metals such as Cd and Pb) at high pH may be linked to dissolution of SOM at high pH (i.e. increased DOM: Fig. S4), as it is known to be strongly associated with DOM (Fan et al. 2021).

The PTEs Cd, Pb, Zn were grouped with Mn into Cluster 4, which was characterized by large highly-reactive fractions in the single-step extractions with dilute HCl or HNO3 (> 0.8 except for Zn) and was distinct from other clusters by the large fraction (0.4– 0.7) of acetic acid/acetate (pH 4.5)-extractable metal (Fig. 3). This latter pool is interpreted as a pH-sensitive metal pool, such as metal monosulfides and carbonates (Tessier et al. 1979; Poulton and Canfield 2005). Previous work has shown pH-sensitive nature of particulate Cd, Zn, Pb in urban rainwater runoff and river sediments (Wiseman 1985; Morrison et al. 1990). In line with the results from the (sequential) extraction protocols, the pH-leaching experiment showed extensive metal release into solution under low pH (Fig. 6). However, the model results indicate that Cd, Pb and Zn are mostly associated with Fe/Al (oxyhydr)oxides and SOM (Fig. S7), from which these PTEs are desorbed under low pH. From our results, it is not obvious why the metals in Cluster 4, which based on modeling have a similar speciation as other PTEs, would have a high acetate/acetic acid (pH 4.5)-extractable fraction. Previous work has also found this fraction to be an important pool of Cd, Pb and Zn in sediments (Šurija and Branica 1995), without being able to explain why these PTEs specifically would be 'carbonate-associated'. Even though the sequential extraction and pH-leaching experiment yield similar results, the nature of the pH-sensitive

metal pool remains uncertain. Regardless of the underlying mechanism, the pH-sensitive nature of these PTEs makes them potentially mobile in response to perturbations such as oxidation and acidification induced by dredging activities. With regard to the low solubility of metals from clusters 2, 3 and 4 at high pH (Fig. 6), we note that some sample oxidation during times the pH was adjusted could have contributed to the pool of iron (oxyhydr)oxides that may adsorb the investigated PTEs (Fig. S7). The uptick in dissolved metal concentrations at the highest pH indicates that such a potential artefact was, however, of limited importance and did not affect results or conclusions.

4.3 Implications

Understanding the behavior and fate of contaminants in dredged sediments is crucial for sustainable sediment management. By combining chemical extractions with pH-leaching experiments and multi-surface sorption modeling, we provide insight into metal pools in sediments from the heavily human-impacted estuarine environment of Europe's largest harbor, the Port of Rotterdam. Because harbors worldwide are faced with similar challenges concerning sediment removal and disposal (Piou et al. 2009; Förstner and Salomons 2010), our results are more widely applicable. Regarding the implications of our findings, we note that sediments throughout the Port of Rotterdam show heavy metal concentrations that are mostly below Dutch intervention values. Earlier work already indicated a marked decrease in metal contamination in PoR sediments since the 1990s (Salomons 2005). Regarding sediment contamination, there has been a shift from metal contamination to pollution with organic (micro)pollutants in recent times (Ahmed et al. 2020).

Nonetheless, heavy metals are enriched in many, river-dominated areas of the Port of Rotterdam compared to natural sediment. Furthermore, other harbors or strongly human-impacted estuarine/coastal ecosystems worldwide contain sediments that are still strongly contaminated with heavy metals (Zeng et al. 2022; Naik et al. 2023) and subject to perturbations such as natural sediment resuspension and dredging. Our results indicate that the reactivity and potential mobility of heavy metals in such contaminated sediments is strongly dependent on metal species. Specifically, we found that the heavy metals Cd, Co, Cu, Pb and Zn have relatively high reactive fractions (> 50% of total metal) and can thus be expected to have high mobility under specific environmental conditions (Cappuyns and Swennen 2008; Zhang et al. 2014). Regarding mobility, we further note that the multi-surface sorption modeling indicated that the highly reactive metal fractions occurred predominantly as Fe/Al (oxyhydr) oxide- and SOM-adsorbed species; adsorption is reversible and thus these metals can be released through competition, for instance as a result of salinity or pH changes. The leaching patterns suggested a sharp release of Pb, Cd, and Zn when pH drops from 8 to 5. Such a degree of acidification was reported to occur within 8–20 weeks under simulated deposition on land (Cappuyns and Swennen 2011). From the perspective of sediment management, sediments should therefore be viewed not as a permanent sink, but rather a significant temporal storage, especially for metals with high sensitivity to environmental changes.

The multi-surface sorption model, although initially developed to study soil metal mobility, showed a good performance in capturing the metal release patterns for the investigated sediments. One of the key advantages of this model is its process-based feature, which explicitly considers ion binding to heterogeneous reactive surfaces, distinguishes between electrostatic and ion-specific binding mechanisms, and accounts for competition between ions. This, combined with its use of generic parameters that have been derived over a wide domain of conditions (e.g. pH, ionic strength) makes it a robust research tool for application beyond soils (Groenenberg et al. 2012), proving useful in diverse environments like acid-main-drainage (Butler et al. 2008) and waste materials like bottom ash of municipal solid wastes (Dijkstra et al. 2008).

Dredged sediment can evolve into soil once deposited on land, making the application of this geochemical model particularly relevant. The model has demonstrated strong performance for cations within a pH range of 3–8 across most soils (Groenenberg et al. 2012), which aligns well with the pH levels observed in sediments during oxidation (Cappuyns and Swennen 2011). Nevertheless, implementing additional processes could further enhance the model's predictive accuracy for sediment, especially under changing conditions. Examples of processes include (1) metals that bind to sulfides and carbonates, which may become mobilized during sediment oxidation and acidification; (2) the oxidation of OM might alter humic substance concentrations, a critical input for the model; (3) the changes of Al/Fe/Mn-(oxyhydr)oxide concentrations. Although the current model demonstrated a good performance, suggesting that these processes might have limited impact on metal leaching in the investigated sediments, further insight to these processes is needed to reduce the model uncertainty, particularly when it is used for risk assessment of materials different from soils.

5 Conclusions

- The mobility of metals within the PoR sediments displayed large variability due to the diverse metal sources and their intrinsic binding properties. Generally, metal contents were relatively higher in silt, OM-rich riverine sediments. Some PTEs (e.g. Cd, Pb, Zn, Cu, Cr) enriched in the low salinity environment were possibly contributed from human activities in the urban area and historical PTE residues in the sediments.
- Although the total amount cannot be translated into metal mobility, three independent extractions consistently suggested certain anthropogenic PTEs (i.e. Cd, Pb, Zn) were present in highly reactive forms, such as carbonates, AVS and labile (oxyhydr)oxides. This resulted in their sensitivity to even slight sediment acidification, witnessed in the pH-dependent leaching experiments. In contrast, geogenic metals (e.g. Cr, Ni, Co), largely incorporated into clay minerals or pyrites/OM-bound, were recalcitrant or poorly reactive.
- The potential metal mobility depends on the inherent reactivity of associated minerals (i.e. four clusters) as well as the depositional conditions (e.g. pH, redox potential). The leaching behaviors of PTEs showed strong pH-dependent patterns. Although our results do not explicitly reveal the chemical nature of the pH-sensitive metal pool, it is crucial to acknowledge that sediment disturbance (e.g. dredging) can lead to oxidation and acidification, which may alter metal availability. Hence, comprehensive characterization of sediments, together with their depositional environments, is indispensable for metal mobility prediction.

Supplementary Information The online version contains supplementary material available at https://doi.org/10.1007/s11368-024-03936-1.

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Data availability The datasets used in this study are available from the corresponding author upon reasonable request.

Declarations

Competing interests The authors declare no competing interests.

References

Ahmed MB, Johir MAH, McLaughlan R et al (2020) Per- and polyfluoroalkyl substances in soil and sediments: occurrence, fate, remediation and future outlook. Sci Total Environ 748:141251. https://doi.org/10.1016/j.scitotenv.2020.141251

Aller RC (1998) Mobile deltaic and continental shelf muds as suboxic, fluidized bed reactors. Mar Chem 61:143–155. https://doi.org/10.1016/S0304-4203(98)00024-3

Anderson LD, Delaney ML (2000) Sequential extraction and analysis of phosphorus in marine sediments: streamlining of the SEDEX procedure. Limnol Oceanogr 45:509–515. https://doi.org/10.4319/lo.2000.45.2.0509

Biggs RB (1970) Sources and distribution of suspended sediment in northern Chesapeake Bay. Mar Geol 9:187–201. https://doi.org/10.1016/0025-3227(70)90014-9

Brady JP, Kinaev I, Goonetilleke A, Ayoko GA (2016) Comparison of partial extraction reagents for assessing potential bioavailability of heavy metals in sediments. Mar Pollut Bull 106:329–334. https://doi.org/10.1016/j.marpolbul.2016.03.029

Brand E, Peijnenburg W, Groenenberg B et al (2009) Towards implementation of bioavailability measurements in the Dutch regulatory framework. RIVM, Bilthoven

Burton ED, Bush RT, Sullivan LA (2006) Fractionation and extractability of sulfur, iron and trace elements in sulfidic sediments. Chemosphere 64:1421–1428. https://doi.org/10.1016/j.chemosphere.2005.12.003

Butler BA, Ranville JF, Ross PE (2008) Observed and modeled seasonal trends in dissolved and particulate Cu, Fe, Mn, and Zn in a mining-impacted stream. Water Res 42:3135–3145. https://doi.org/10.1016/j.watres.2008.03.004

Canfield DE, Raiswell R, Bottrell S (1992) The reactivity of sedimentary iron minerals toward sulfide. Am J Sci 292:659–683. https://doi.org/10.2475/ajs.292.9.659

Cappuyns V (2012) A critical evaluation of single extractions from the SMT program to determine trace element mobility in sediments. Appl Environ Soil Sci 2012. https://doi.org/10.1155/2012/672914

Cappuyns V, Swennen R (2008) The application of pHstat leaching tests to assess the pH-dependent release of trace metals from soils, sediments and waste materials. J Hazard Mater 158:185–195. https://doi.org/10.1016/j.jhazmat.2008.01.058

Cappuyns V, Swennen R (2011) Oxidation of anoxic soils and sediments: how can we evaluate the risk of heavy metal release? In: Ramsey G, McHugh S (eds) River Sediments. Nova Science Publishers, Hauppauge, pp 77–101

Choi KY, Kim SH, Chon HT (2012) Relationship between total concentration and dilute HCl extraction of heavy metals in sediments of harbors and coastal areas in Korea. Environ Geochem Health 34:243–250. https://doi.org/10.1007/s10653-011-9425-z

Claff SR, Sullivan LA, Burton ED, Bush RT (2010) A sequential extraction procedure for acid sulfate soils: partitioning of iron. Geoderma 155:224–230. https://doi.org/10.1016/j.geoderma.2009.12.002

Couvidat J, Neculita CM, Benzaazoua M et al (2017) Evaluation of biogeochemical reactivity of fresh and weathered contaminated dredged sediments. J Soils Sediments 17:543–556. https://doi.org/10.1007/s11368-016-1578-z

Crocetti P, González-Camejo J, Li K et al (2022) An overview of operations and processes for circular management of dredged sediments. Waste Manag 146:20–35. https://doi.org/10.1016/j.wasman.2022.04.040

Dijkstra J, Meeussen J, Comans R (2004) Leaching of heavy metals from contaminated soils: an experimental and modeling study. Environ Sci Technol 38:4390–4395

Dijkstra JJ, Meeussen JCL, Van der Sloot HA, Comans RNJ (2008) A consistent geochemical modelling approach for the leaching and reactive transport of major and trace elements in MSWI bottom ash. Appl Geochem 23:1544–1562. https://doi.org/10.1016/j.apgeochem.2007.12.032

Dijkstra JJ, Meeussen JCL, Comans RNJ (2009) Evaluation of a generic multisurface sorption model for inorganic soil contaminants. Environ Sci Technol 43:6196–6201. https://doi.org/10.1021/es900555g

Du Laing G, De Vos R, Vandecasteele B et al (2008) Effect of salinity on heavy metal mobility and availability in intertidal sediments of the Scheldt estuary. Estuar Coast Shelf Sci 77:589–602. https://doi.org/10.1016/j.ecss.2007.10.017

Dyer KR (1995) Sediment Transport Processes in Estuaries. In: Perillo GME(ed) Geomorphology and Sedimentology of Estuaries. Elsevier, Amsterdam, pp 423–449

Dzombak DA, Morel FMM (1991) Surface complexation modeling: hydrous ferric oxide. John Wiley & Sons, New York

Fan X, Liu C, Yu X et al (2021) Insight into binding characteristics of copper(II) with water-soluble organic matter emitted from biomass burning at various pH values using EEM–PARAFAC and two-dimensional correlation spectroscopy analysis. Chemosphere 278:130439. https://doi.org/10.1016/j.chemosphere.2021.130439

Förstner U, Salomons W (2010) Sediment research, management and policy: a decade of JSS. J Soils Sediments 10:1440–1452. https://doi.org/10.1007/s11368-010-0310-7

Gao H, Koopmans GF, Song J et al (2022) Evaluation of heavy metal availability in soils near former zinc smelters by chemical extractions and geochemical modelling. Geoderma 423:115970. https://doi.org/10.1016/j.geoderma.2022.115970

Gil-Díaz T, Schäfer J, Filella M et al (2019) Fractionation of inherited and spiked antimony (sb) in fluvial/estuarine bulk sediments: unexpected anomalies in parallel selective extraction protocols. Appl Geochem 108:104386. https://doi.org/10.1016/j.apgeochem.2019.104386

Griffioen J, Klaver G, Westerhoff WE (2016) The mineralogy of suspended matter, fresh and cenozoic sediments in the fluvio-deltaic Rhine-Meuse-Scheldt-Ems area, the Netherlands: an overview and review. Geol en Mijnbouw/Netherlands J Geosci 95:23–107. https://doi.org/10.1017/njg.2015.32

Groenenberg JE, Lofts S (2014) The use of assemblage models to describe trace element partitioning, speciation, and fate: a review. Environ Toxicol Chem 33:2181–2196. https://doi.org/10.1002/etc.2642

Groenenberg JE, Dijkstra JJ, Bonten LTC et al (2012) Evaluation of the performance and limitations of empirical partition-relations and process based multisurface models to predict trace element solubility in soils. Environ Pollut 166:98–107. https://doi.org/10.1016/j.envpol.2012.03.011

Groenenberg JE, Römkens PFAM, Zomeren A, Van et al (2017) Evaluation of the single dilute (0.43 M) nitric acid extraction to determine geochemically reactive elements in soil. Environ Sci Technol 51:2246–2253. https://doi.org/10.1021/acs.est.6b05151

Hiemstra T, de Wit JCM, Van Riemsdijk WH (1989) Multisite proton adsorption modeling at the solid/solution interface of (hydr) oxides: a new approach: II. Application to various important (hydr)oxides. J Colloid Interface Sci 133:105–117. https://doi.org/10.1016/0021-9797(89)90285-3

Hu S, Tao C, Liao S et al (2022) Transformation of minerals and mobility of heavy metals during oxidative weathering of seafloor massive sulfide and their environmental significance. Sci Total Environ 819. https://doi.org/10.1016/j.scitotenv.2022.153091

IJsseldijk LL, Camphuysen KCJ, Nauw JJ, Aarts G (2015) Going with the flow: tidal influence on the occurrence of the harbour porpoise (Phocoena phocoena) in the Marsdiep area, the Netherlands. J Sea Res 103:129–137. https://doi.org/10.1016/j.seares.2015.07.010

ISO TC/190 (2012c) Soil quality – Parameters for geochemical modelling of leaching and speciation of constituents in soils and materials – Part 3: Extraction of aluminium oxides and hydroxides with ammonium oxalate/oxalic acid. ISO 12782-3:2012. ISO, Geneva

ISO/TC 190 (2012a) Soil quality – Parameters for geochemical modelling of leaching and speciation of constituents in soils and materials – Part 1: Extraction of amorphous iron oxides and hydroxides with ascorbic acid. ISO 12782-1:2012. ISO, Geneva

ISO/TC 190 (2012b) Soil quality – Parameters for geochemical modelling of leaching and speciation of constituents in soils and materials – Part 2: Extraction of crystalline iron oxides and hydroxides with dithionite. ISO 12782-2:2012. ISO, Geneva

ISO/TC 190 (2016) Soil quality – Extraction of trace elements using dilute nitric acid. ISO 17586:2016. ISO, Geneva.

Jilbert T, Asmala E, Schröder C et al (2018) Impacts of flocculation on the distribution and diagenesis of iron in boreal estuarine sediments. Biogeosciences 15:1243–1271. https://doi.org/10.5194/bg-15-1243-2018

Job T, Penny D, Morgan B (2020) Geochemical signatures of acidic drainage recorded in estuarine sediments after an extreme drought. Sci Total Environ 749:141435. https://doi.org/10.1016/j.scitotenv.2020.141435

Keon NE, Swartz CH, Brabander DJ et al (2001) Validation of an arsenic sequential extraction method for evaluating mobility in sediments. Environ Sci Technol 35:2778–2784. https://doi.org/10.1021/es001511o

Kinniburgh DG, Van Riemsdijk WH, Koopal LK et al (1999) Ion binding to natural organic matter: competition, heterogeneity, stoichiometry and thermodynamic consistency. Colloids Surf Physicochem Eng Asp 151:147–166. https://doi.org/10.1016/S0927-7757(98)00637-2

Kirichek A, Rutgers R, Wensween M, van Hassent A (2018) Sediment management in the Port of Rotterdam. Baggern - Unterbringen - Aufbereiten - Verwerten. Steinbeis-Transverzentrum Angewandte Landschaftsplanung, pp 1–8

Kraal P, Burton ED, Bush RT (2013) Iron monosulfide accumulation and pyrite formation in eutrophic estuarine sediments. Geochim Cosmochim Acta 122:75–88. https://doi.org/10.1016/j.gca.2013.08.013

Kraal P, Bostick BC, Behrends T et al (2015) Characterization of phosphorus species in sediments from the Arabian Sea oxygen minimum zone: combining sequential extractions and X-ray spectroscopy. Mar Chem 168:1–8. https://doi.org/10.1016/j.marchem.2014.10.009

Król A, Mizerna K, Bożym M (2020) An assessment of pH-dependent release and mobility of heavy metals from metallurgical slag. J

Hazard Mater 384. https://doi.org/10.1016/j.jhazmat.2019.121502
Larner BL, Palmer AS, Seen AJ, Townsend AT (2008) A comparison of an optimised sequential extraction procedure and dilute acid leaching of elements in anoxic sediments, including the effects of oxidation on sediment metal partitioning. Anal Chim Acta 608:147–157. https://doi.org/10.1016/j.aca.2007.12.016
Leleyter L, Rousseau C, Biree L, Baraud F (2012) Comparison of EDTA, HCl and sequential extraction procedures, for selected metals (Cu, Mn, Pb, Zn), in soils, riverine and marine sediments. J Geochemical Explor 116–117:51–59. https://doi.org/10.1016/j.gexplo.2012.03.006
McLachlan RL, Ogston AS, Allison MA (2017) Implications of tidally-varying bed stress and intermittent estuarine stratification on fine-sediment dynamics through the Mekong's tidal river to estuarine reach. Cont Shelf Res 147:27–37. https://doi.org/10.1016/j.csr.2017.07.014
Meeussen JCL (2003) Orchestra: an object-oriented framework for implementing chemical equilibrium models. Environ Sci Technol 37:1175–1182. https://doi.org/10.1021/es025597s
Meima JA, Comans RNJ (1998) Application of surface complexation/precipitation modeling to contaminant leaching from weathered municipal solid waste incinerator bottom ash. Environ Sci Technol 32:688–693. https://doi.org/10.1021/es9701624
Miranda LS, Wijesiri B, Ayoko GA et al (2021) Water-sediment interactions and mobility of heavy metals in aquatic environments. Water Res 202:117386. https://doi.org/10.1016/j.watres.2021.117386
Mol G, Spijker J, van Gaans P, Romkens P (2012) Geochemische Bodematlas Van Nederland. Wageningen Academic, Wageningen
Morgan B, Rate AW, Burton ED (2012) Trace element reactivity in FeS-rich estuarine sediments: influence of formation environment and acid sulfate soil drainage. Sci Total Environ 438:463–476. https://doi.org/10.1016/j.scitotenv.2012.08.088
Morrison GMP, Revitt DM, Ellis JB (1990) Metal speciation in separate stormwater systems. Water Sci Technol 22:53–60
Murthy MK, Khandayataray P, Samal D (2022) Chromium toxicity and its remediation by using endophytic bacteria and nanomaterials: a review. J Environ Manage 318:115620. https://doi.org/10.1016/j.jenvman.2022.115620
Mymrin V, Stella JC, Scremim CB et al (2017) Utilization of sediments dredged from marine ports as a principal component of composite material. J Clean Prod 142:4041–4049. https://doi.org/10.1016/j.jclepro.2016.10.035
Naik S, Pradhan U, Karthikeyan P et al (2023) Ecological risk assessment of heavy metals in the coastal sediment in the South-Western Bay of Bengal. Front Mar Sci 10. https://doi.org/10.3389/fmars.2023.1255466
Patricia M, Koopal LK, Huclier S (2006) Modeling metal–particle interactions with an emphasis on natural organic matter. Environ Sci Technol 40:7459–7466. https://doi.org/10.1021/es0628203
Piou S, Bataillard P, Laboudigue A et al (2009) Changes in the geochemistry and ecotoxicity of a zn and cd contaminated dredged sediment over time after land disposal. Environ Res 109:712–720. https://doi.org/10.1016/j.envres.2009.04.009
Poulton SW, Canfield DE (2005) Development of a sequential extraction procedure for iron: implications for iron partitioning in continentally derived particulates. Chem Geol 214:209–221. https://doi.org/10.1016/j.chemgeo.2004.09.003
Rodrigues SM, Henriques B, da Silva EF et al (2010) Evaluation of an approach for the characterization of reactive and available pools of twenty potentially toxic elements in soils: part I - the role of key soil properties in the variation of contaminants' reactivity. Chemosphere 81:1549–1559. https://doi.org/10.1016/j.chemosphere.2010.07.026
Römkens PF, Guo HY, Chu CL et al (2009) Characterization of soil heavy metal pools in paddy fields in Taiwan: Chemical extraction and solid-solution partitioning. J Soils Sediments 9:216–228. https://doi.org/10.1007/s11368-009-0075-z
Sakan S, Franciskovic-Bilinski S, Dordevic D et al (2021) Evaluation of element mobility in river sediment using different single extraction procedures and assessment of probabilistic ecological risk. Water 13. https://doi.org/10.3390/w13101411
Salomons W (2005) Sediments in the catchment-coast continuum - dedicated to Prof. Dr. Ulrich Forstner on his 65th birthday. J Soils Sediments 5:2–8. https://doi.org/10.1065/jss2005.01.0129
Steele JH, Thorpe SA, Turekian KK (2010) Marine Chemistry & Geochemistry. Academic Press, Amsterdam
Šurija B, Branica M (1995) Distribution of cd, pb, Cu and Zn in carbonate sediments from the Krka river estuary obtained by sequential extraction. Sci Total Environ 170:101–118. https://doi.org/10.1016/0048-9697(95)04607-3
Tessier A, Campbell PGC, Bisson M (1979) Sequential extraction procedure for the speciation of particulate trace metals. Anal Chem 51:844–851. https://doi.org/10.1021/ac50043a017
van der Sloot HA, van Zomeren A, Meeussen JCL et al (2007) Test method selection, validation against field data, and predictive modelling for impact evaluation of stabilised waste disposal. J Hazard Mater 141:354–369. https://doi.org/10.1016/j.jhazmat.2006.05.106
van der Veer G (2006) Geochemical soil survey of the Netherlands. Dissertation, Utrecht University
van Zomeren A, Comans RNJ (2007) Measurement of humic and fulvic acid concentrations and dissolution properties by a rapid ratch procedure. Environ Sci Technol 41:6755–6761. https://doi.org/10.1021/es0709223
Vermaat J, Bouwer L, Turner K, Salomons W (2005) Managing European coasts Past, Present and Future. Springer, Berlin
Vink JPM, van Zomeren A, Dijkstra JJ, Comans RNJ (2017) When soils become sediments: large-scale storage of soils in sandpits and lakes and the impact of reduction kinetics on heavy metals and arsenic release to groundwater. Environ Pollut 227:146–156. https://doi.org/10.1016/j.envpol.2017.04.016
Vollprecht D, Riegler C, Ahr F et al (2020) Sequential chemical extraction and mineralogical bonding of metals from styrian soils. Int J Environ Sci Technol 17:3663–3676. https://doi.org/10.1007/s13762-020-02694-0
Vos H, Janssen M (2008) EU-wide control measures to reduce pollution from WFD relevant substances. Copper and zinc in the Netherlands. RIVM, Bilthoven
Wiseman LP (1985) Speciation of Heavy Metals in Highway Drainage Systems. Dissertation, University of Central Florida
Zeng J, Han G, Zhang S, Zhang Q (2022) Suspended sediments quality assessment in a coastal river: identification of potentially toxic elements. Int J Environ Res Public Health 19. https://doi.org/10.3390/ijerph19074293
Zhang C, Yu Z, gang, Zeng G et al (2014) ming, Effects of sediment geochemical properties on heavy metal bioavailability. Environ Int 73:270–281. https://doi.org/10.1016/j.envint.2014.08.010
Zimmerman AJ, Weindorf DC (2010) Heavy metal and trace metal analysis in soil by sequential extraction: a review of procedures. Int J Anal Chem 2010:1–7. https://doi.org/10.1155/2010/387803