

Effect of salinity on heavy metal mobility and availability in intertidal sediments of the Scheldt estuary

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Abstract

The effect of the flood water salinity on the mobility of heavy metals was studied for intertidal sediments of the Scheldt estuary (Belgium). Soils and sediments of 4 sampling sites were flooded with water of different salinities (0.5, 2.5, and 5 g NaCl L⁻¹). Metal concentrations were monitored in pore water and surface water. To study the potential effects of flood water salinity on metal bioavailability, duckweed (*Lemna minor*) was grown in the surface water. The salinity was found to primarily enhance the mobility of Cd and its uptake by duckweed. Cadmium concentrations in pore water of soils and sediments and surrounding surface waters significantly exceeded sanitation thresholds and quality standards during flooding of initially oxidized sediments. Moreover, the effect was observed already at lower salinities of 0.5 g NaCl L⁻¹. This implies that risks related to Cd uptake by organisms and Cd leaching to ground water are relevant when constructing flooding areas in the brackish zones of estuaries. These risks can be reduced by inducing sulphide precipitation because Cd is then immobilised as sulphide and its mobility becomes independent of flood water salinity. This could be achieved by permanently flooding the polluted sediments, because sulphates are sufficiently available in the river water of the brackish part of the estuary.

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1. Introduction

Due to industrial and urban development, a significant amount of the intertidal flats in the Scheldt estuary is contaminated with heavy metals. Sediments and their associated plant litter are expected to be major sinks for metals (Du Laing et al., 2006, 2007a). Metal binding in the sediments is determined by input coming from discharge of industrial and urban sewage or by atmospheric deposition in the catchment, but also by the extent to which the sediment is capable to bind and release metals. This is governed by soil and sediment characteristics such as pH, cation exchange capacity and organic matter content, redox conditions and chloride content.

These properties determine metal sorption and precipitation processes, which are also related to the metal mobility, bioavailability and potential toxicity (Du Laing et al., 2002). Increasing organic matter and clay contents (Du Laing et al., 2007a) and sulphide contents (Du Laing et al., in preparation) were previously found to enhance metal accumulation in the intertidal Scheldt sediments, whereas higher salinities resulted in reduced metal accumulation (Du Laing et al., 2007a). As such, varying salinities are expected to affect metal mobility in the intertidal sediments and have a major impact on their bioavailability as previously demonstrated in soil-dwelling spiders (Du Laing et al., 2002).

Results of both laboratory (Paalman et al., 1994) and field experiments (Hatje et al., 2003) have demonstrated an increasing metal mobilisation with increasing salinities. This is especially the case for Cd, since chlorocomplexation decreases the activity of free Cd²⁺ in the soil solution and increases desorption

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(Paalman et al., 1994; Hatje et al., 2003). The Cd speciation shifts towards CdCl^+ , CdCl_2 , CdCl_3^- and CdCl_4^{2-} forms (Helmké, 1999). Salinity effects are not confined to the complexation capacity of salt anions. When Ca^{2+} and Mg^{2+} are abundant in the soil solution, metals will also be mobilised from particles as a result of competition between these divalent cations and the metal ions (Paalman et al., 1994). These driving forces are important for Zn and Cd in particular (Millward and Liu, 2003). Such effects of salinity on metal mobility have been studied extensively in upland soils and estuarine surface waters (e.g. for the Scheldt estuary by Van Eck, 1999 and Gerringa et al., 2001). However, studies of the effects of changing salinity on metal fate in intertidal sediments have been scarce. On the one hand, this can be attributed to a lack of easy methods for pore water extraction and metal speciation, mobility and availability assessment under actual moisture regimes, as pointed out by Meers et al. (2006). On the other hand, a lack of knowledge of the kinetics of metal release and immobilisation processes which occur under changing redox conditions hampers a straightforward interpretation of analyses results (Du Laing et al., 2007b). Understanding the factors which determine metal mobility in intertidal flats can however contribute to a more sustainable development of wetland ecosystems and can help to evaluate whether and under which conditions wetland creation is a safe option. The current paper focuses on assessing the potential effects of intertidal sediment flooding on metal mobility in the Scheldt estuary as a function of the salinity of the flood water.

Studying the effect of salinity on the metal mobility in intertidal sediments and soils is particularly important for the Scheldt estuary as a major flooding area is currently being constructed in the brackish zone. To protect a major part of the estuarine population from flooding during storm tides, floodplains are often most effective in these brackish zones compared to upstream areas. Moreover, the number of floodplains will probably increase and the salinity gradient is expected to move upstream in the future due to the expected sea level rising. The latter is also expected to induce a shift from alternately flooded towards permanently flooded conditions and thus result in a shrinking of the intertidal surface area. Moreover, we previously found that the metal mobility in intertidal clayey sediments with relatively short (<2 days) emerged periods after each period of flooding tends towards the metal mobility in permanently flooded conditions (Du Laing et al., 2007b). As such conditions mainly occur in the freshwater and brackish marshes of the Scheldt estuary, we only focussed on permanent flooding in this study and refer to Du Laing et al. (2007b) for the effect of flooding regime on metal mobility.

2. Materials and methods

2.1. Study area

The Scheldt takes its rise in the north of France in the vicinity of St.-Quentin, at a height of 100 m above sea level. It runs through Belgium, crosses the border between Belgium and

The Netherlands and discharges into the North Sea near Vlissingen (The Netherlands) about 355 km downstream. Similar to other estuaries, a longitudinal salinity gradient can be observed along the Scheldt river. The salinity of the Scheldt river water decreases from the sea up to the mouth of the tributary Durme, where chloride concentrations stabilize around 100 mg L^{-1} in the surface water. The longitudinal salinity profile is primarily determined by the magnitude of river discharge, whereas the tidal action contributes to a lesser degree. As a result, significant salinity variations in the surface water are observed. The lower riverine part from Ghent to Antwerp is a tidal fresh water river during winter and spring, whereas the water becomes brackish between Antwerp and the Rupel mouth during summer and autumn (Baeyens et al., 1998).

A surface area of 1 m^2 of soil or sediment was scooped homogeneously up to a depth of 30 cm at 4 sampling sites: Kramp ($51^\circ 3.101' \text{N}$, $4^\circ 9.457' \text{E}$), Kijkverdriet ($51^\circ 7.268' \text{N}$, $4^\circ 17.786' \text{E}$), Galgenschuur ($51^\circ 18.228' \text{N}$, $4^\circ 17.276' \text{E}$) and Lippensbroek ($51^\circ 5.1135' \text{N}$, $4^\circ 10.846' \text{E}$). The sites were selected based on known and quantifiable levels of the metals of interest, and varying characteristics and physico-chemical properties. Kramp, Kijkverdriet and Galgenschuur are intertidal marshes, which are regularly flooded by Scheldt river water. Galgenschuur is situated in the brackish part of the Scheldt estuary, whereas Kramp is situated in the freshwater part. Kijkverdriet is situated at the boundary between the freshwater and the brackish zone. Lippensbroek is situated between Kramp and Kijkverdriet. It was a polder at the time of sampling, but it is now being used as a pilot controlled flooding area. To improve readability, the soil sampled at Lippensbroek, which probably also originated from sediment deposition before the area was impoldered a long time ago, will hereafter be referred to as 'sediment', when it is mentioned together with the sediments of other sampling sites. The salinity of the flood water at the sampling sites varies from about 0.7 near Kramp to 5.5 near Galgenschuur.

2.2. Experimental setup

Plant roots and litter were removed from the sampled sediments. To homogenize the sediment, it was sieved over a sieve of 8 mm mesh width and intensively mixed. The fraction larger than 8 mm was discarded. The homogeneous sediment was distributed over 3 polyethylene recipients of $32 \times 24 \times 20 \text{ cm}$, as every sediment was subjected to 3 treatments. Every recipient was provided with a sediment layer of 11 cm thick. The recipients were stored in a greenhouse at a temperature controlled between 15 and 25 °C and a light regime of 16 h light per day. The recipients were flooded with water of 3 different salinities for 250 days. Water was added until the water level was situated at 5 cm above the sediment surface. Solutions of the desired salinity were prepared by dissolving NaCl in deionised water in amounts of 0.5 (low salinity), 2.5 (middle salinity) and 5 g NaCl L^{-1} (high salinity), respectively. These treatments and their salinities will be referred to as 0.5, 2.5 and 5. Different amounts of flood water were added to the sediments to reach saturation as the sediments were characterised by different initial

water contents and densities. As a result, the salinities of the sediments which were finally reached, differed. Therefore, Na and Cl^- contents in the pore water were monitored extensively as they are expected to affect metal fate. Evaporation and removal by sampling were compensated for by adding deionised water weekly to ensure that water levels were maintained at 5 cm above the sediment surface without affecting total salt amounts in the recipients. This amounted on average to about 0.5 L of distilled water per recipient each week. While sampling resulted in removal of some salts from the experimental setup, this effect was minor since only approximately 10% of the initially added water and salt amounts were removed during the 8-month experiment. It was not feasible to duplicate the experimental setup as we aimed to conduct the experiment with different salinities and types of sediments, meanwhile maintaining a relatively high temporal sampling resolution. Therefore, the effect of sediment heterogeneity was diluted by duplicating the sampling procedure (see Section 2.3).

To study the effect of salinity on metal bioavailability, duckweed (*Lemna minor*) was transplanted to the recipients around day 150. After a growth period of 4 weeks, the plants were harvested and analysed for metal contents.

2.3. Sampling

Each container was fitted with four 10 cm Rhizon MOM soil moisture samplers (Eijkelpamp, Giesbeek, NL) to extract pore water and surface water in vacuum tubes over a porous filter compartment with a pore size of 0.1 μm . Two samplers were installed horizontally at 5 cm below the sediment surface to sample pore water. The two other samplers were installed to sample surface water at 2.5 cm above the sediment surface, coinciding with 2.5 cm below the water surface (Fig. 1). To install them, holes were made in the recipient walls, through which the samplers were injected into the sediment. Silicone was used to ensure that all connections were waterproof. The procedure to extract and simultaneously filter the pore water has already been used successfully when studying the influence of the hydrological regime on pore water metal concentrations in a contaminated sediment-derived soil (Du Laing et al., 2007b). During the first 140 days of the experiment, pore water of the sediments was extracted by both Rhizon samplers approximately twice a week. Four extra samples

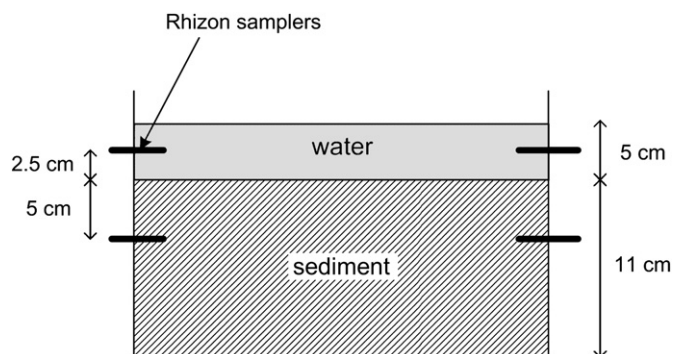


Fig. 1. Experimental setup.

were taken at days 184, 232, 246 and 248. Surface water was extracted 9 times during the entire experiment, using the two Rhizon samplers installed above the sediment surface. The samples were acidified with concentrated HNO_3 to keep the metals in solution and to solubilise metals which precipitated during sampling. Samples of both samplers were poured together in a recipient and stored in a refrigerator before analysis.

During filling of the recipients, three samples were taken of the sediment of each recipient to analyse the physico-chemical sediment properties. Around days 150 and 250, two core samples were taken from the sediment of each recipient to check for possible changes in these physico-chemical sediment properties during the experiment. Therefore, a cylindrical PVC tube (diameter 5 cm) was hammered in the sediment. Subsequently, the sediment was removed from the tube with a spoon. To homogenise the sediments preceding the analyses, they were dried overnight at 70 °C and ground in a hammer-cross beater mill. This was however not done for the determination of acid volatile sulphide (AVS) contents, as drying can cause oxidation of the sulphides.

2.4. Analyses

All glassware and containers used were washed in a laboratory dishwasher, subsequently soaked overnight in 5% ultrapure 65% HNO_3 and rinsed with deionised water. Pseudo-total metal contents in the sediments were determined by an aqua regia destruction (Ure, 1990) and analysed with ICP-OES (Varian Vista MPX, Varian, Palo Alto, CA). Acid volatile sulphide (AVS) was determined on fresh sediment samples by transformation of sulphide into H_2S and absorption in a Zn-acetate solution, followed by a back titration. This method is described by Tack et al. (1997). The pH was measured in a 1/5 sediment/distilled water suspension after an equilibration of 18 h (Van Ranst et al., 1999). The conductivity was measured in the filtrate of a 1/5 sediment/distilled water suspension, shaken for 1/2 h (Van Ranst et al., 1999). The organic matter content was determined by measuring the weight loss after incineration of oven-dried samples (2 h at 450 °C). The carbonate content was determined by back-titration (with 0.5 M NaOH) of an excess 0.25 M H_2SO_4 added to 1 g of sediment (Nelson, 1982). Texture was determined at the Research Institute for Nature and Forest (INBO) using laser diffraction (Coulter LS200, Miami, FL) after removing organic matter and carbonates by adding hydrogen peroxide and an acetate buffer solution respectively. To determine the chloride content 10 g of sediment was suspended in 50 ml of 0.15 M HNO_3 and shaken for 30 min. The filtrate was titrated with 0.05 M AgNO_3 using potentiometric end-point detection (Van Ranst et al., 1999). The cation exchange capacity (CEC) was measured by percolation of 150 ml 1 M NH_4OAc through a percolation tube filled with a mixture of 5 g sediment and 35 g quartz sand, followed by washing through the excess with 300 mL denatured ethanol. The exchangeable ammonium ions were then eluted with 500 mL 1 M KCl and analysed in the percolate by means of a steam distillation (Tecator Kjeltect System 1002 Distilling Unit). The exchangeable cations were

also analysed in this percolate using ICP-OES (Varian Vista MPX, Varian, Palo Alto, CA) (Van Ranst et al., 1999).

All pore water samples were analysed for Cd, Cu, Ni, Fe, Mn and Zn using GF-AAS (Varian SpectraAA-800/GTA-100, Varian, Palo Alto, CA) and ICP-OES (Varian Vista MPX, Varian, Palo Alto, CA). At least every two weeks during the first 140 days, a sample was also analysed for Ca, Mg, Na and K contents. The TOC-, NO_3^- , SO_4^{2-} and Cl^- contents were regularly determined on non-acidified samples directly after sampling. TOC contents in the surface and pore water samples were measured with a TOC-analyser (TOC-5000, Shimadzu, Tokyo Japan). Cl^- contents were determined by titration with 0.05 M AgNO_3 using potentiometric end-point detection. NO_3^- and SO_4^{2-} contents were measured with a Metrohm configuration consisting of a 761 Compact Ion Chromatograph equipped with a 788 IC Filtration Sample Processor and an anion exchange column (IC-AN-Column Metrosep A supp 4, Metrohm Ion Analysis, Switzerland). The surface water samples were also analysed for Cd, Cu, Ni, Fe, Mn, Zn, Ca, Mg, Na, K, TOC, NO_3^- , SO_4^{2-} and Cl^- using the procedures mentioned above. For quality control, standards were always re-analysed at the end of each batch of analyses. The analyses results were only accepted when the measured standard concentrations were within 95–105% of the certified value (i.e. taking into account possible artifacts due to the dilution of certified stock solutions). To check whether the operational metal analyses procedures could be affected by the salinities under investigation, standards were prepared in solutions of 0.5, 2.5 and 5 g NaCl L^{-1} and analysed after calibration with non-saline standards. Results for all metals were found to decrease with increasing salinities in a range from 1 up to 10%, which should be taken into consideration when interpreting the results.

The redox potential of the sediments was measured with a HI 3090 B/5 electrode that was inserted permanently into the sediment. One electrode was placed in each recipient at 5 cm below the sediment surface. For each measurement, the electrode was connected to a HI 9025 meter of HANNA instruments. During the first four months, the redox potential was measured daily, afterwards twice a week. The measured value was corrected to the Standard Hydrogen Electrode as a reference by adding the difference between the redox potential measured in a ZoBells solution (0.033 M $\text{K}_3\text{Fe}(\text{CN})_6$ and 0.033 M $\text{K}_4\text{Fe}(\text{CN})_6$ in 0.1 M KCl) and the theoretical value of +428 mV.

The duckweed plants were analysed in their entirety for metal contents without separating roots from leaves. They were thoroughly rinsed with distilled water and dried overnight at 50 °C. About 0.5 g of plant material was weighed into a beaker and 5 ml of ultra pure HNO_3 were added. The beaker was heated on a hot plate at 130 °C for one hour. After heating, a total of 4 ml H_2O_2 was added to each sample and then heated for 10 min. The suspensions were filtered in 50 ml volumetric flasks using filter papers (S&S blue ribbon, Schleicher & Schuell). The filtrates were diluted to the mark using 1% HNO_3 . Cd, Cu, Ni, Zn, Fe and Mn contents were determined using GF-AAS (Varian SpectraAA-800/GTA-100, Varian, Palo Alto, CA) and ICP-OES (Varian Vista MPX, Varian, Palo Alto, CA).

Multi-factor analysis of variance (ANOVA) (SPSS 12.0) was used to assess the significance of the effects of salinity and sulphides on the metal concentrations in the pore water ($\alpha = 0.05$). Pearson correlations were calculated between metal concentrations in the pore water or surface water and these in the plants. All statistical analyses were performed using SPSS 12.0 (SPSS Inc. Chicago, IL).

3. Results and discussion

3.1. Sediment properties

The Cd, Cu, Ni, and Zn content and the physico-chemical properties of the sediments and the sanitation thresholds and background values for nature areas according to the Flemish legislation (Vlarebo, 1996) are presented in Table 1. Clay and organic matter contents were highest in Kijkverdriet, which also resulted in the highest CEC. CaCO_3 concentrations ranged from 7.9 to 9.2% and accounted for a pH in the neutral to slightly alkaline range (7.33–8.02). Chloride contents and conductivity rapidly decreased when moving upstream from Galgenschoor over Kijkverdriet to Kramp, coinciding with the decreasing influence of salty seawater. As the sediments were excavated during summer, those of Kijkverdriet were also subject to flooding by brackish river water and contain a relatively high chloride content. Lippensbroek was not flooded by river water, which resulted in chloride concentrations below the detection limit of 0.02 g kg^{-1} . The Kijkverdriet sediment was very clayey and the organic matter content was very high. This resulted in a more reduced state, a much higher initial AVS content and a much lower redox potential. All sediments contained quantifiable levels of the targeted metals. Cadmium concentrations exceeded the background levels for soils according to the Flemish legislation (Vlarebo, 1996) by a factor ranging from 2 to 5. Cu concentrations exceeded them by a factor in the range of 4–5 and Ni by a factor from 2 to 3. Zn concentrations were 4–8 times higher than the background values. Cu, Ni and Zn concentrations did however not exceed the soil sanitation threshold values according to the Flemish legislation (Vlarebo, 1996). Cd concentrations significantly exceeded the sanitation thresholds imposed on nature areas in Kijkverdriet, Kramp and Lippensbroek, whereas these thresholds were just not reached in Galgenschoor.

Between 0.2 and 1.8% of total Ni was found to be in the exchangeable fraction, i.e. in the leachate collected during determination of the cation exchange capacity. This ranged between 0.6 and 2.2% for Cu. Cadmium was predominant in the exchangeable fraction, with 12, 16 and 22% of total Cd for Lippensbroek, Kramp and Galgenschoor, respectively. This was however not the case in Kijkverdriet, where the exchangeable fraction accounted for only 1.9% of the total Cd amount. This might be partly due to the formation of insoluble and stable Cd sulphide precipitates as a result of the highly reduced state (e.g. Salomons et al., 1987; Simpson et al., 2000; Guo et al., 1997; Du Laing et al., 2007b). The low Cd amounts in the exchangeable fraction of the Kijkverdriet sediment might also have been promoted by the very significant abundance of

Table 1

Initial metal concentrations, sanitation threshold and background value according to the Flemish legislation (Vlarebo, 1996) and some physico-chemical properties of the sediments (mean \pm standard deviation, $n = 3$). *Sanitation thresholds and background values depend on the organic matter and clay content

	Galgenschoor	Kijkverdriet	Kramp	Lippensbroek
Cd (mg kg ⁻¹ DM)				
Total measured	4.3 \pm 0.1	11.5 \pm 0.2	11.2 \pm 0.1	8.5 \pm 0.1
Sanitation threshold*	5.4	8.3	6.0	5.5
Background value*	2.1	3.3	2.4	2.2
Cu (mg kg ⁻¹ DM)				
Total measured	82 \pm 1	132 \pm 3	125 \pm 1	95 \pm 0
Sanitation threshold*	279	339	311	306
Background value*	24	29	27	26
Ni (mg kg ⁻¹ DM)				
Total measured	32.2 \pm 0.3	53.8 \pm 0.6	40.2 \pm 0.1	32.6 \pm 0.3
Sanitation threshold*	193	275	212	199
Background value*	17	25	19	18
Zn (mg kg ⁻¹ DM)				
Total measured	413 \pm 4	696 \pm 10	947 \pm 7	696 \pm 1
Sanitation threshold*	1140	1623	1231	1149
Background value*	118	168	127	119
Clay (%)	32.4 \pm 1.2	49.4 \pm 0.9	41.5 \pm 0.8	39.9 \pm 0.3
Silt (%)	48.1 \pm 1.1	43.6 \pm 0.5	40.1 \pm 0.9	45.4 \pm 0.6
Sand (%)	19.5 \pm 0.2	7.1 \pm 1.1	18.4 \pm 1.3	14.7 \pm 0.8
CaCO ₃ (%)	7.9 \pm 0.4	8.9 \pm 0.1	9.2 \pm 0.3	7.9 \pm 0.1
OM (%)	15.4 \pm 0.1	28.8 \pm 0.3	15.1 \pm 0.6	12.2 \pm 0.4
pH	7.93 \pm 0.05	7.33 \pm 0.00	8.02 \pm 0.01	7.63 \pm 0.06
EC (μ S cm ⁻¹)	3970 \pm 61	1058 \pm 15	216 \pm 15	85 \pm 1
Cl ⁻ (g kg ⁻¹ DM)	71.29 \pm 0.18	10.19 \pm 0.47	0.62 \pm 0.03	<0.02 \pm 0.00
CEC (cmol(+) kg ⁻¹)	22.9 \pm 0.3	37.7 \pm 1.0	28.2 \pm 0.0	27.0 \pm 0.4
AVS (mg kg ⁻¹ DM)	45 \pm 17	995 \pm 216	42 \pm 37	51 \pm 63
Redox (mV)	+465 \pm 28	-168 \pm 8	+457 \pm 17	+470 \pm 19

Mn in this fraction. While only 0.2–1.0% of the total Mn was found to be exchangeable in the sediments of Lippensbroek, Kramp and Galgenschuur, this percentage amounted to 9.1 in Kijkverdriet. As Cd tends to form stable and insoluble sulphides, soluble Mn created upon reduction of the Kijkverdriet sediment probably replaces Cd at negatively charged sediment surfaces. Zn is also quite well represented in the exchangeable fractions of the sediments of Galgenschuur and Kramp (4.3 and 3.3%), whereas it is less abundant in exchangeable fractions of the sediments of Kijkverdriet and Lippensbroek (0.9 and 1.0%).

Most physico-chemical sediment properties did not change significantly during the first 150 days of the experiment. However, some remarkable shifts in the Lippensbroek soil were observed. CaCO₃ concentrations decreased from 7.9 \pm 0.1 to 5.1 \pm 0.4%, whereas organic matter concentrations also decreased from 12.2 \pm 0.4 to 9.5 \pm 0.2%. A relatively fast decomposition of organic matter probably results in proton release and dissolution of the carbonates, which in turn might affect metal mobility (van den Berg and Loch, 2000; Du Laing et al., 2007b). These effects were also observed to a smaller extent in the sediments of Galgenschuur and Kramp, whereas they were not significant in the Kijkverdriet sediment.

3.2. Salinity of the pore water

For the middle and high salinity treatments, average chloride and sodium concentrations in the pore water were lower

in the treatments of Kramp and Kijkverdriet, compared to Lippensbroek (Table 2). Differences were thus observed between the salinity of the pore water and the salinity of the flood water, which has also been observed in field conditions by Lau and Chu (1999). The lower initial water content in Lippensbroek implied that a greater amount of saline water had to be added to reach saturated conditions. Chloride and sodium concentrations were highest in the pore water of the Galgenschuur sediment, where they were also less affected by the salinity of the flood water. This could be attributed to the higher initial salinity as this sediment originated from the brackish part of the estuary. TOC concentrations were quite variable (Table 2), but no significant differences between treatments could be observed.

3.3. Metal concentrations in the pore water

Fe and Mn concentrations in the pore water are plotted as a function of time in Fig. 2. In Kijkverdriet, Fe and Mn concentrations were already high at the start of the experiment, and subsequently decreased. The highly reduced state of the Kijkverdriet sediment at the time of sampling probably implies the dominance of Fe/Mn-oxides reducing microbial colonies (Lovley and Phillips, 1988b), which promoted rapid reduction of Fe/Mn-oxides and formation of soluble Fe²⁺ and Mn²⁺, as previously observed (Du Laing et al., 2007b). The decrease in Fe and Mn concentrations in the pore water may be due to continuing formation of insoluble Fe- and

Table 2
 Cl⁻, Na and TOC concentrations in the pore water of 4 different sediments flooded with water of salinities 0.5, 2.5 and 5 (mean of samples taken at different sampling times ± standard deviation, *n* = 10 for Cl⁻, 15 for Na and 8 for TOC)

Sediment	Treatment	Cl ⁻ (g L ⁻¹)	Na (g L ⁻¹)	TOC (mg L ⁻¹)
Galgenschoor	Low salinity	4.16 ± 0.67	2.06 ± 0.33	5.9 ± 2.4
	Middle salinity	4.60 ± 0.80	2.32 ± 0.4	5.7 ± 1.3
	High salinity	5.68 ± 0.80	2.68 ± 0.39	6.6 ± 1.4
Kijkverdriet	Low salinity	0.44 ± 0.05	0.20 ± 0.02	11.6 ± 6.9
	Middle salinity	0.81 ± 0.07	0.35 ± 0.05	13.2 ± 7.1
	High salinity	1.40 ± 0.17	0.65 ± 0.09	14.9 ± 5.1
Kramp	Low salinity	0.21 ± 0.01	0.12 ± 0.02	4.3 ± 1.5
	Middle salinity	0.84 ± 0.07	0.35 ± 0.09	3.5 ± 2.2
	High salinity	1.45 ± 0.19	0.61 ± 0.15	5.4 ± 1.8
Lippensbroek	Low salinity	0.26 ± 0.02	0.08 ± 0.01	3.4 ± 2.8
	Middle salinity	1.28 ± 0.12	0.46 ± 0.05	6.7 ± 2.4
	High salinity	3.01 ± 0.30	1.03 ± 0.09	9.2 ± 2.6

Mn-sulphides during sulphate reduction. Sulphides were abundant in the Kijkverdriet sediment from the beginning of the experiment (Table 1). The hypothesis of continuing sulphide formation was also confirmed by the redox potentials (Fig. 3). In the Kijkverdriet sediment, the low redox potential at the beginning of the experiment (−168 mV) points to favourable conditions for sulphate reduction. The further decrease during the first 10 days of the experiment towards a quite stable value in the range of −260 to −280 mV indicated that Fe and Mn oxide reduction probably ended. Mn concentrations however suddenly increased around day 250. Due to the very high evaporation rates as a result of increased temperatures at that moment, the water table level lowered significantly in a very short time. Moreover, a lot of fresh water had to be added to compensate this evaporation. As a result, increased oxygen concentrations probably resulted in a rapid oxidation of Mn-sulphides.

In Galgenschoor, Kramp and Lippensbroek, Mn concentrations first increased, followed by a decrease. The increase could be attributed to the activity of Fe/Mn oxides reducing microbial communities and resulting formation of soluble Mn²⁺ and Fe²⁺. The solubilisation of Mn started directly after the beginning of the experiment. A peak was reached between day 50 and day 150, after which the Mn concentrations started to decrease. Significant Fe mobilisation only started after a lag period of about 50 days, which coincided with the period of increasing Mn concentrations. Some authors, such as Lovley and Phillips (1988a), have previously reported that the reduction of Fe³⁺ does not begin before all Mn⁴⁺ is depleted. In the Lippensbroek soil however, Fe mobilisation started at the beginning of the experiment. This upland soil probably contains more easily reducible types of Fe-oxides and/or less easily reducible types of Mn-oxides. The Fe concentrations started to decrease after day 175 in the pore water of Kramp and Lippensbroek, whereas they keep increasing in the pore water of Galgenschoor. The decreases in the second part of the experiment (after day 100) could be attributed to the formation of insoluble Fe- and Mn-sulphides upon reduction of sulphates, which probably takes the upper hand. This hypothesis is strengthened by the observation of decreasing sulphate contents (Fig. 4) accompanied by a decrease in redox potentials

(Fig. 3). No significant sulphate reduction was expected to occur in the beginning of the experiment, based on the initially high redox potentials (+465, +466 and +470 mV for Galgenschoor, Kramp and Lippensbroek, respectively). During the experiment, redox potentials decreased to reach a final values in the range of −250 to −280 mV (Fig. 3). The rate of the decrease depended upon the treatment. In all Kramp sediments, the decrease was rather gradual and the −150 mV value was not reached before day 60. This redox value is expected to coincide with dominating sulphate reduction, according to Gambrell et al. (1991). The redox potential already reached −150 mV between day 10 and day 20 in the Lippensbroek soil, with the decrease rate slowing down afterwards. A similar evolution was observed in the Galgenschoor sediment, but the period of fast redox potential decrease lasted until day 20–40.

The faster decrease of redox potentials in Galgenschoor compared to Kramp is reflected in the peak of Mn contents being reached earlier. Mn concentrations of Lippensbroek however did not decrease as fast as in Kramp or Galgenschoor regardless the fast decreases of the redox potential to below −150 mV. This is probably due to the lower sulphate availability (Fig. 4), which might be limiting for sulphide formation. Some authors, such as Salomons et al. (1987) previously reported limited sulphate reduction in freshwater environments, due to the lower sulphate availability. The hypothesis of sulphide formation is confirmed by an increase of up to 200 mg AVS kg⁻¹ DM in the sediment of Galgenschoor after 250 days, coinciding with the significantly decreasing sulphate concentrations in solution (Fig. 4). It is however not confirmed for the sediments of Kramp and Lippensbroek, as no significant sulphide formation was detected. For a 10 mg L⁻¹ decrease of Fe or Mn concentrations in the pore water, a sulphide production of about 6 mg S²⁻ L⁻¹ pore water is needed. The method which was used to detect AVS was not sensitive enough to correctly detect such low concentrations, as the detection limit was about 10 mg S²⁻ kg⁻¹ sediment. Not only increasing sulphide formation, but also decreasing availability of easily reducible Mn-oxides is expected to facilitate the decrease of Mn concentrations in the pore water. According to Salomons et al. (1987), the lower sulphate concentrations in freshwater environments may result in only a partial transformation of the iron hydroxides to iron

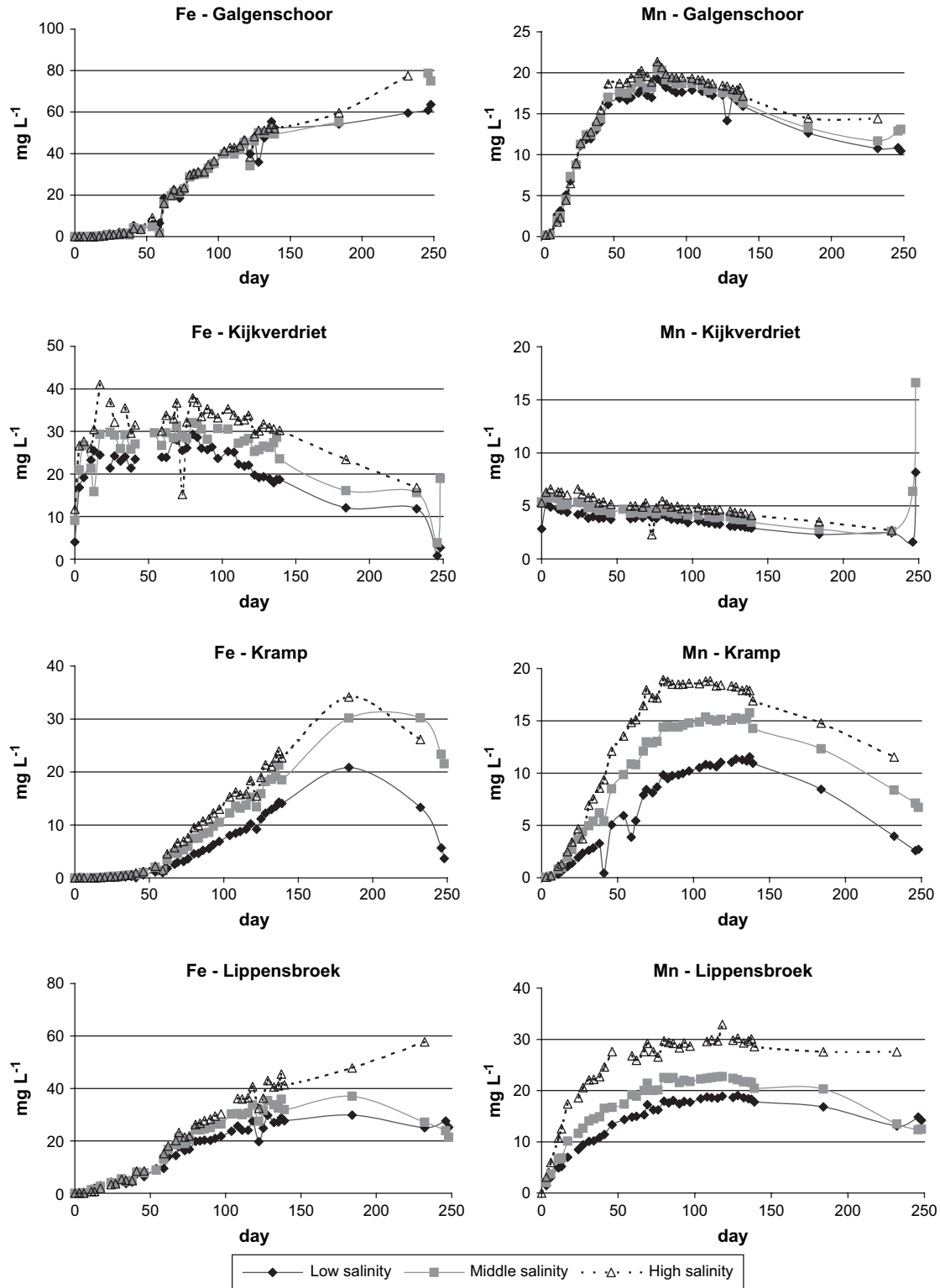


Fig. 2. Change in redox potential of four different sediments flooded with water of three different salinities (low = 0.5, middle = 2.5, high = 5) as a function of time.

sulphides, whereas the methanogenic state is reached relatively fast and part of the available reducible iron is converted to siderite (FeCO₃).

Fe and Mn mobilisation are both significantly facilitated by increasing salinity. The effects of salinity on Fe and Mn

mobility were significant for the sediments of Kijkverdriet and Kramp ($p < 0.001$ for Fe and Mn in Kijkverdriet, $p < 0.001$ for Mn in Kramp and $p = 0.039$ for Fe in Kramp). For the Lippensbroek soil, the effect of salinity on the Mn mobility was significant at the 0.001 level, but the effect on the Fe

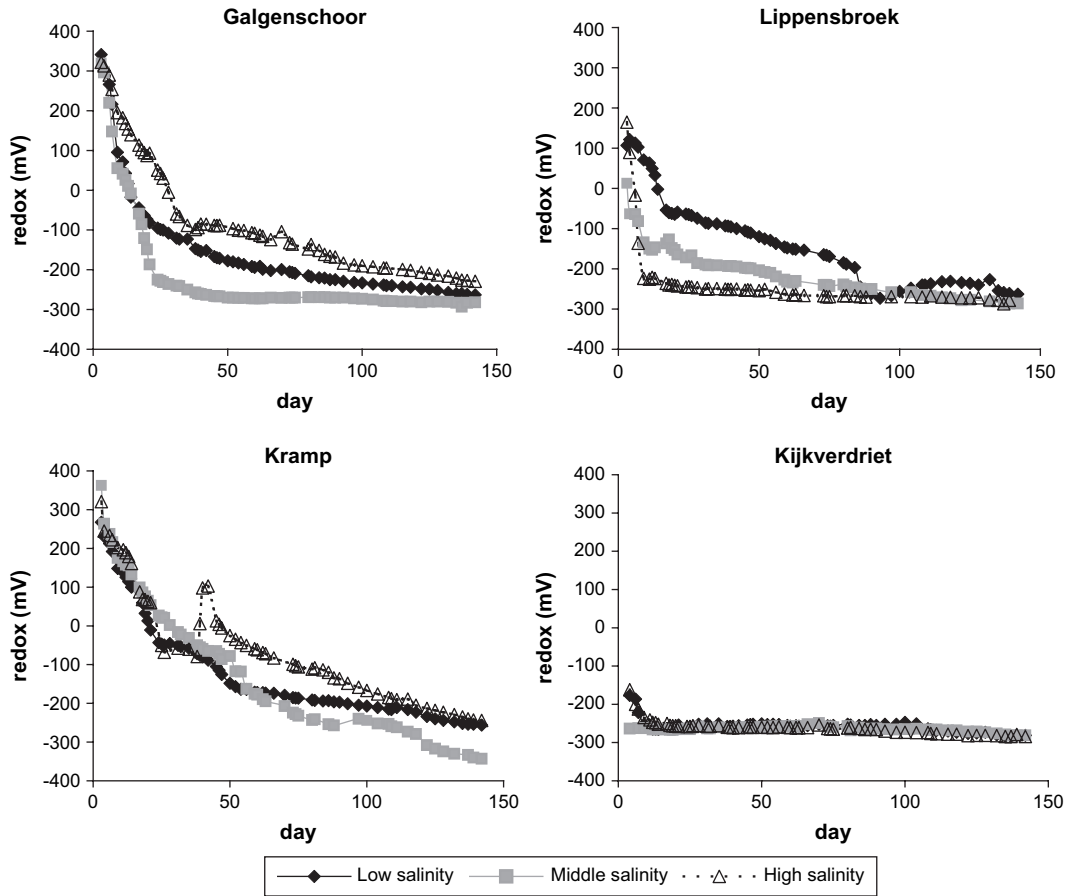


Fig. 3. Change in Fe and Mn pore water concentrations (mg L^{-1}) of four different sediments flooded with water of three different salinities (low = 0.5, middle = 2.5, high = 5) as a function of time.

mobility was not significant ($p = 0.085$). Furthermore, salt addition does not significantly affect Fe and Mn mobility in the Galgenschoor sediment ($p = 0.995$ and $p = 0.461$, respectively), which was already very saline before adding the saline flood water (Table 2). According to Khattak et al. (1989), salt addition did not significantly affect the reduction of Mn

oxides, but it induces a pH decrease. In combination with reducing conditions, this low pH creates a favourable environment for solubilisation of Mn, whereas $\text{Mn}^{2+}\text{-Ca}^{2+}/\text{Na}^+$ exchange reactions prevent the sorption of Mn to soil particles. Free Mn will immediately form soluble MnCl_2 in the presence of chlorides (Khattak et al., 1989; Hatje et al., 2003).

Cd concentrations in the pore water of the different sediments are plotted as a function of sampling time in Fig. 5. In the reduced, sulphide-rich sediment of Kijkverdriet, Cd concentrations in the pore water continuously remained below the Flemish background level of $1 \mu\text{g L}^{-1}$. This can be attributed to the fact that Cd-sulphides are highly insoluble (e.g. Salomons et al., 1987; Zumdahl, 1992; Simpson et al., 2000; Guo et al., 1997). In the initially oxidised sediments, increasing Cd concentrations are observed during the first 20 days. This is followed by a rapid decrease until day 50, after which the Cd concentrations remained very low.

The Cd concentrations in the pore waters of Galgenschoor and Kramp rapidly decreased to below the background value of $1 \mu\text{g L}^{-1}$. For the Lippensbroek soil however, it took about 150 days to reach the background value. The peak concentrations, which were reached before day 20, often significantly exceeded the Flemish remediation standard for ground water ($5 \mu\text{g L}^{-1}$). The decreasing concentrations in the second part of the experiment can be attributed to Cd-sulphide formation.

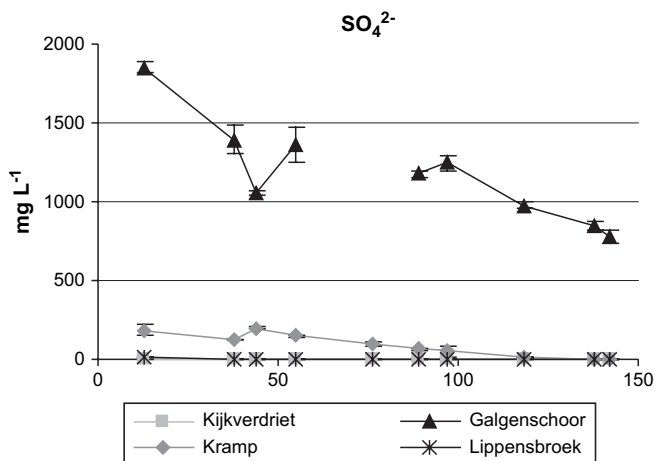


Fig. 4. Change in SO_4^{2-} pore water concentrations of the sediments of Kijkverdriet, Galgenschoor, Kramp and Lippensbroek (mean of all salinity treatments \pm standard deviation).

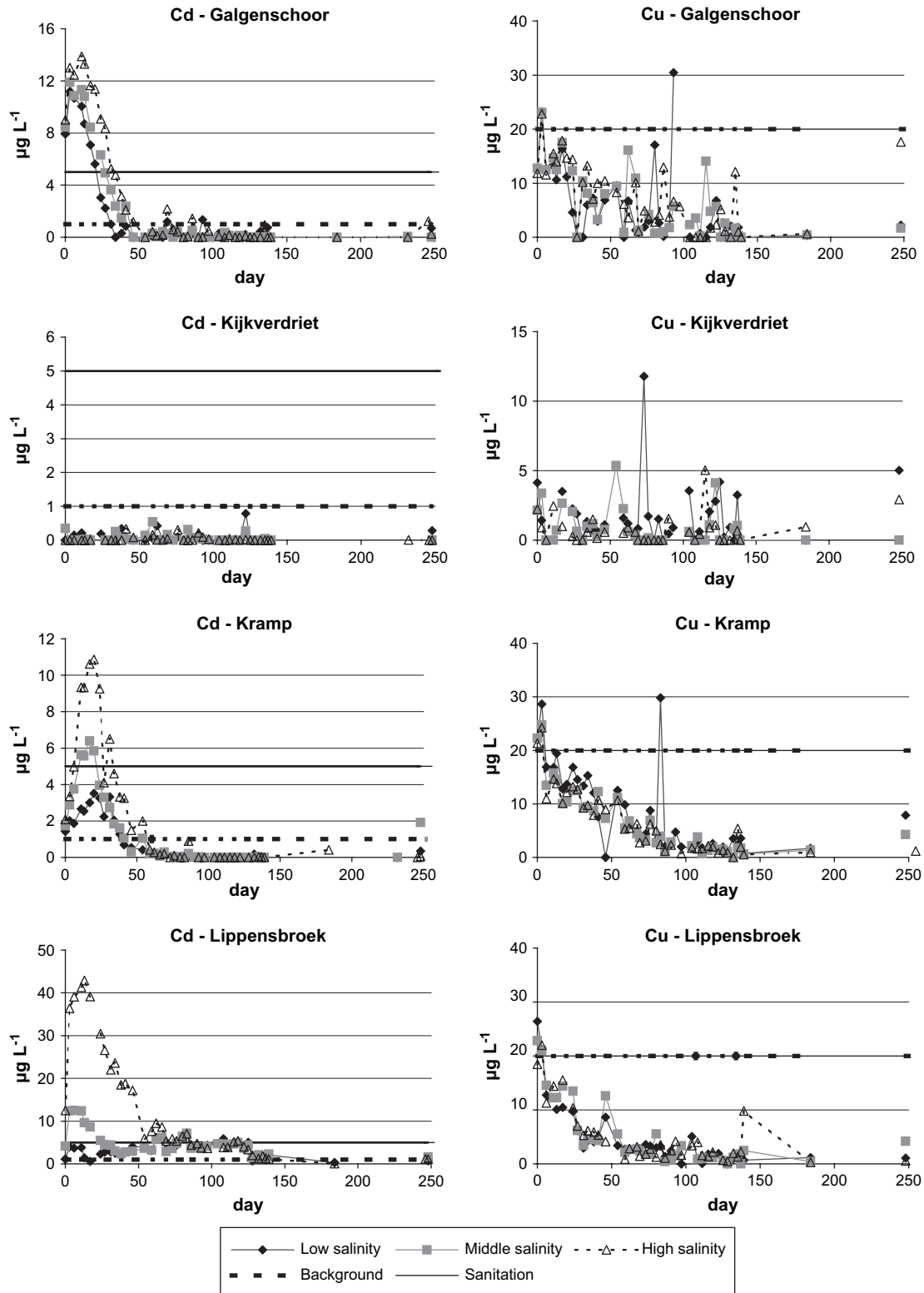


Fig. 5. Change in Cd and Cu pore water concentrations ($\mu\text{g L}^{-1}$) of four different sediments flooded with water of three different salinities (low = 0.5, middle = 2.5, high = 5) as a function of time; background levels and sanitation thresholds for groundwater according to Vlarebo (1996).

This hypothesis is strengthened by the fact that background values were not easily reached in the Lippensbroek soil after day 50. In that soil, sulphide formation was probably hampered due to the low sulphate availability (Fig. 4).

The Cd concentrations were primarily affected by the salinity of the flood water in Kramp ($p = 0.030$) and Lippensbroek ($p < 0.001$), the sediments from the freshwater part of the estuary that initially were oxidised. Increasing salinity clearly

resulted in an increasing Cd mobility. This has also been reported by other authors (Paalman et al., 1994; Hatje et al., 2003). It also corroborates earlier findings by Gerringa et al. (2001). They found that high salinities resulted in a faster release of Cd from CdS during the oxidation of reduced Scheldt sediments. This release was found to be stimulated by both formation of chloride complexes and ion exchange. The effect is most significant in the Lippensbroek soil ($p < 0.001$), for which the salinity treatment caused a very strong increase in salinity of the pore water compared to the sediments natural conditions. A Cd concentration of up to $45 \mu\text{g L}^{-1}$, which coincides with 9 times the sanitation threshold, was observed after flooding with high salinity water. Even when the Lippensbroek soil was subjected to a salinity of only $0.5 \text{ mg NaCl L}^{-1}$, the remediation threshold was regularly exceeded. This suggests that subjecting polluted freshwater sediments or soils to a saline environment may, at least temporarily, create a significant environmental hazard. Increasing the salinity of the flood water of the already saline Galgenschoor sediment did however not influence Cd mobility significantly ($p = 0.393$), but it also did not affect the salinity of the pore water, as has previously been discussed. In contrast with the mobility of Fe and Mn, Cd mobility in the Kijkverdriet sediment was not significantly affected by the salinity ($p = 0.254$), probably because of the much lower solubility of Cd sulphides compared to sulphides of Fe and Mn (Zumdahl, 1992). When Kijkverdriet was classified as being sulphide-rich and all other sites as being sulphide-poor, a multiple ANOVA with salinity and sulphide classification as independent variables indeed indicates a significant interaction between sulphides and salinity ($p = 0.014$) on the pore water Cd concentration. Sulphide abundance and formation thus obviously interferes with the effect of salinity on Cd mobility.

To confirm this, the highest observed Cd concentration in the pore water of each treatment during the first 50 days was also plotted as a function of the average Cl^- concentration in the pore water (Fig. 6). The decreasing slope of the linear regression curve from Lippensbroek towards Kijkverdriet indeed suggests that the effect of pore water salinity on Cd mobility decreases when sulphides are abundant or being formed. Kijkverdriet sediment initially contained a significant amount

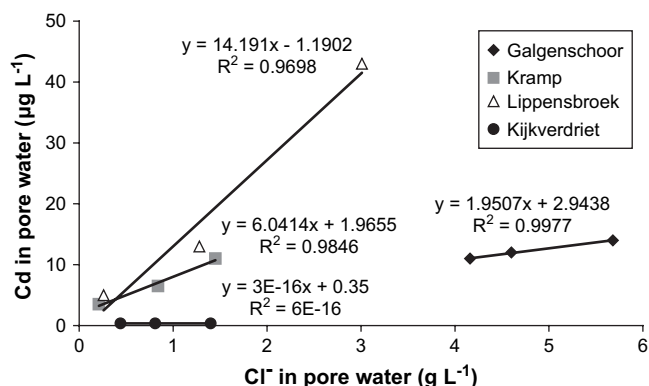


Fig. 6. Highest observed Cd concentration in the pore water of each treatment during the first 50 days plotted as a function of the average Cl^- concentration in the pore water.

of sulphides, which explains the low and constant Cd concentrations in the sediment solution that are largely unaffected by salinity. Contrarily, the largest effect of salinity on Cd mobility was observed for Lippensbroek, where sulphate availability was limiting for sulphide formation. Sulphides were initially not detected in Kramp, but were slowly being formed during sulphate reduction (Fig. 4). This increasing effect of sulphides might explain the somewhat smaller salinity effect in this sediment. In the Galgenschoor sediment, sulphides were rapidly being formed (Fig. 4), which resulted in an even lower effect of salinity, and thus a smaller slope compared to the one of Kramp. The suppression of salinity effects on metal mobility in the abundance of sulphides was already observed by Salomons et al. (1987). They calculated the influence of the sulphide concentration on the speciation and solubility of Zn, Cu and Cd in a solution with a chlorinity of 5000 mg L^{-1} and an alkalinity of 50 meq L^{-1} . The effect of the presence of chlorides on the solubility of Cd, Cu and Zn was indeed only observed at low sulphide concentrations.

The Cu concentrations in the pore water rarely exceeded background levels (Fig. 5). They were lowest in the initially reduced sediment of Kijkverdriet and exhibited a decreasing trend with time in the sediments which were initially more oxidised. Contrary to Cd, pore water Cu concentrations started to decrease from the beginning of the experiment. This might be due to the lower solubility product of Cu sulphides (Zumdahl, 1992) but also to the strong association of Cu with organic matter (e.g. Kalbitz and Wennrich, 1998; Alvim Ferraz and Lourenço, 2000), of which the decomposition rate significantly decreases under more reducing conditions (e.g. Reddy and Patrick, 1975). Moreover, coinciding with the evolution of redox potentials, the decrease of Cu contents was slowest in Kramp, which suggests that the decreasing trend is indeed initiated by sulphide formation. Moreover, Cu concentrations reach very low values in the Lippensbroek soil after day 50, which was not observed for Cd. This might again be attributed to the lower solubility product of Cu-sulphides compared to Cd-sulphides, which especially becomes important in conditions of limiting sulphate availability (Fig. 4). Indeed, contrary to Cd, salinity does not significantly affect Cu mobility ($p = 0.600, 0.357$ and 0.878 for Galgenschoor, Kramp and Lippensbroek, respectively). This could be due to the lower stability of Cu-chloride complexes combined with the lower solubility product of Cu-sulphides, which would both explain a lower Cu solubility. A significant salinity effect is observed in the Kijkverdriet sediment ($p = 0.029$), but this is rather meaningless, since most data were very close to the detection limit of $2 \mu\text{g L}^{-1}$.

Ni concentrations increased from the beginning of the experiment in pore water of the initially oxidised sediments (Fig. 7). The evolutions of Ni concentrations are very similar to those of Fe and Mn, which was also observed by Du Laing et al. (2007b) and suggests that Ni is mainly associated with Fe/Mn-oxides. The direct mobilisation after the beginning of the experiment, which was also observed for Mn but not for Fe, and the fact that Ni mobilisation does not accelerate from day 50 in contrast with the Fe mobilisation both suggest

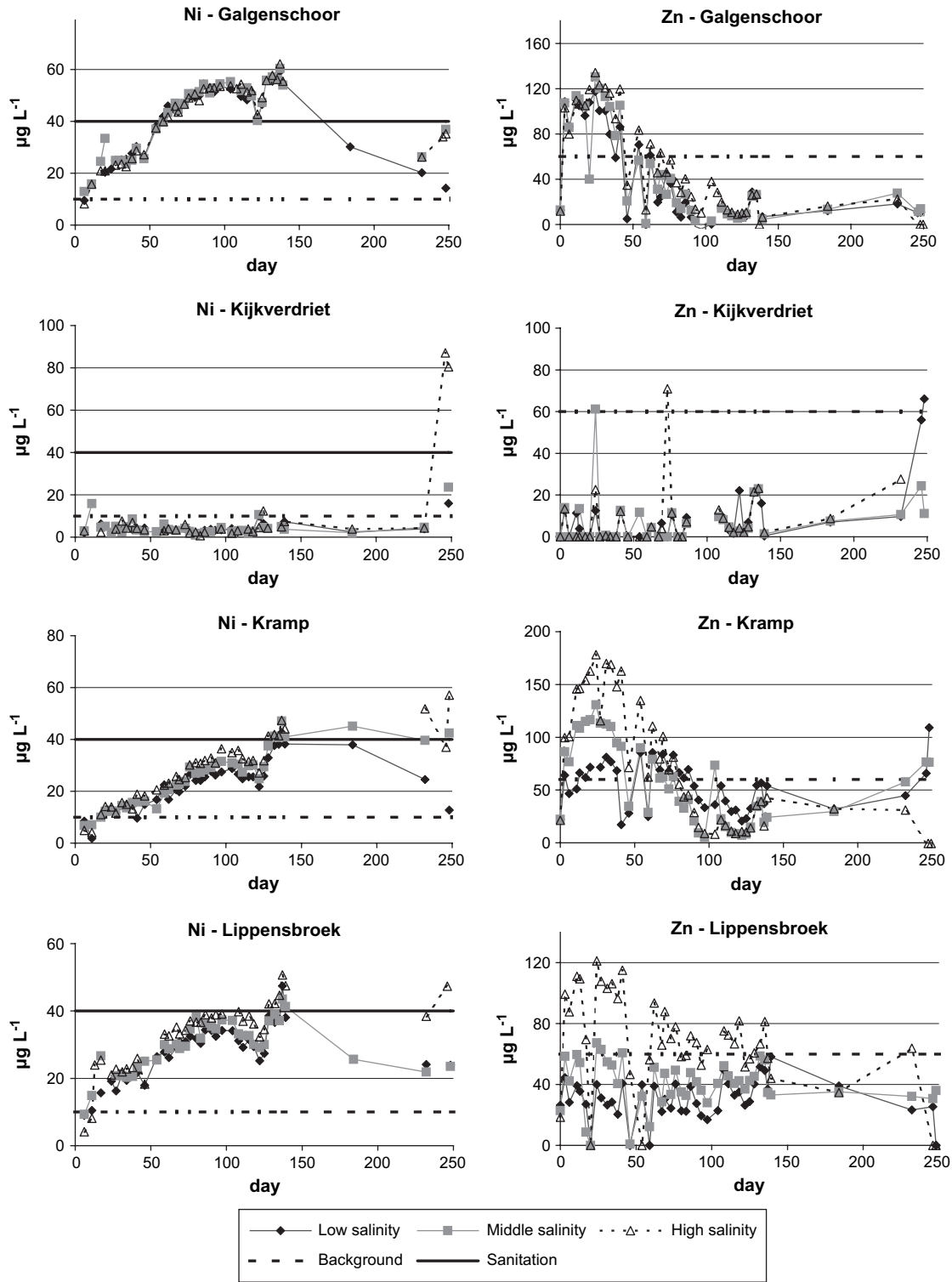


Fig. 7. Change in Ni and Zn pore water concentrations ($\mu\text{g L}^{-1}$) of four different sediments flooded with water of three different salinities (low = 0.5, middle = 2.5, high = 5) as a function of time; background levels and sanitation thresholds for groundwater according to Vlarebo (1996).

that Ni is primarily associated with Mn oxides. Ni was previously reported to primarily co-precipitate with Mn oxides in salt marsh sediments from the Western Scheldt (Zwolsman et al., 1993 in: Callaway et al., 1998). This is also reflected in the lower Pearson correlation coefficient of 0.361 between Ni and Fe compared to 0.781 between Ni and Mn. Whereas

the Mn mobilisation was significantly affected by the salinity, Ni mobility was not ($p = 0.889, 0.159, 0.092$ and 0.060 for Galgenschoor, Kijkverdriet, Kramp and Lippensbroek, respectively). This could be due to a combination of the higher stability of Mn-chlorides compared to Ni-chloride complexes and the lower solubility of Ni-sulphides compared to Mn-sulphides.

The decreasing Ni concentrations in the second part of the experiment may indeed be due to the continuing formation of insoluble Ni-sulphides during the reduction of sulphates (e.g. Salomons et al., 1987; Simpson et al., 2000). Probably for the same reason, the Ni concentrations in pore water of the initially reduced Kijkverdriet sediment were continuously low. They however suddenly increase around day 250. As already mentioned when discussing the evolution of Mn concentrations, oxygen supply due to increased evaporation rates at the end of the experiment probably have lead to a rapid oxidation of sulphides and solubilisation of associated metals. Higher salinities clearly seem to promote this solubilisation.

Zn concentrations generally exceeded background values in the first part of the experiment, but they remained far below the threshold values for sanitation (Fig. 7). They decreased after a relatively small initial increase. Changes over time in pore water Zn concentration are similar to those of Cd, but fluctuations were much larger. According to Millward and Liu (2003), Cd and Zn mobilisation are subject to the same driving forces: chlorocomplexation and competition with Ca, Mg and Na. Their similar mobilisation behaviour is confirmed by the significant Pearson correlation between both metal concentrations in the pore water ($R = 0.490$). Zn concentrations however more slowly decreased in the second part of the experiment, compared to Cd concentrations. This was also observed by Simpson et al. (2000) and can be attributed to the significantly higher solubility of Zn sulphides than Cd sulphides. As for Cd, Fe and Mn, mobilisation was promoted by increasing salinities in sediments originating from the freshwater part of the estuary. For the Lippensbroek soil, this salinity effect was significant ($p < 0.001$). Increasing salinities also promoted Zn mobilisation in the sediment of Kramp during the first 75 days. In the second part of the experiment, however, the highest Zn concentrations were found in the pore water of the low salinity treatment, which caused the overall effect to be evaluated as non-significant in statistical analysis ($p = 0.207$). In the brackish (Galgenschoor) and strongly reduced (Kijkverdriet) sediments, the effects of salinity on the Zn mobility were also not significant ($p = 0.525$ and 0.863 , respectively).

In this experiment, the salinity was reached using NaCl as salt. However, estuarine waters also contain other ions, such as Ca^{2+} , Mg^{2+} and SO_4^{2-} . The presence of double charged cations is expected to increase the metal release under sulphide-poor conditions, whereas the presence of sulphates might promote a faster sulphide precipitation.

3.4. Metal concentrations in the surface water

Cd, Cu and Ni concentrations in the surface water samples and the Flemish surface water quality standards are presented in Table 3. Cd concentrations in the surface water were highly variable and generally lower than in the pore water of the sediments. If contacted with the reduced, sulphide-rich Kijkverdriet sediment, the Cd concentrations meet the quality standard of $1 \mu\text{g L}^{-1}$ defined by the Flemish environmental legislation. However, when sediments from the freshwater part of the estuary were contacted with water of salinities above $2.5 \text{ g NaCl L}^{-1}$, the Cd concentrations in the surface water often significantly exceeded the quality standard, and $42 \mu\text{g L}^{-1}$ was measured once. Similar to pore water Cd concentrations, the concentrations in the surface water are significantly affected by the salinity of the flood water in the initially oxidised, low-salinity sediments ($p < 0.001$ for Lippensbroek and Kramp). They were not significantly affected in the already saline sediment of Galgenschuur ($p = 0.279$) or the sulphide-rich sediment of Kijkverdriet ($p = 0.459$). The temporal variations of Cd concentrations in the surface water and the effect of salinity are clearly demonstrated in Fig. 8. The significant temporal variations can be attributed to the surface water being exposed more to fluctuations in temperature, evapotranspiration, biomass production, etc. compared to the pore water. Zn concentrations rarely exceeded the detection limit and are therefore not presented in Table 3. Cu and Ni concentrations never exceeded their quality standards of $50 \mu\text{g L}^{-1}$. They were subjected to large variations, but they are not significantly affected by salinity. Cu concentrations were significantly lower and Ni concentrations significantly higher in surface water that was in contact with the

Table 3
Cd, Cu and Ni concentrations in the surface water samples of 4 different sediments flooded with water of salinities 0.5, 2.5 and 5 (mean of samples taken at different sampling times \pm standard deviation, $n = 9$) and the Flemish surface water quality standards

Sediment	Treatment	Cd ($\mu\text{g L}^{-1}$)	Cu ($\mu\text{g L}^{-1}$)	Ni ($\mu\text{g L}^{-1}$)
Galgenschoor	Low salinity	0.85 ± 0.53	13.5 ± 4.9	5.7 ± 3.7
	Middle salinity	1.15 ± 0.80	12.6 ± 4.6	5.5 ± 3.6
	High salinity	6.20 ± 13.41	13.4 ± 3.8	12.4 ± 22.7
Kijkverdriet	Low salinity	0.06 ± 0.13	2.6 ± 2.8	9.4 ± 2.7
	Middle salinity	0.15 ± 0.24	3.8 ± 2.5	10.7 ± 3.3
	High salinity	0.25 ± 0.49	4.8 ± 4.9	10.3 ± 3.1
Kramp	Low salinity	0.69 ± 0.41	15.8 ± 6.1	7.6 ± 13.5
	Middle salinity	1.24 ± 0.61	15.4 ± 3.6	5.5 ± 4.0
	High salinity	2.50 ± 1.29	15.4 ± 4.0	3.9 ± 3.8
Lippensbroek	Low salinity	0.57 ± 0.22	16.5 ± 4.3	3.9 ± 2.1
	Middle salinity	1.56 ± 0.54	15.9 ± 4.0	2.4 ± 1.7
	High salinity	4.56 ± 1.95	16.4 ± 5.1	4.2 ± 3.8
Flemish surface water quality standard		1	50	50

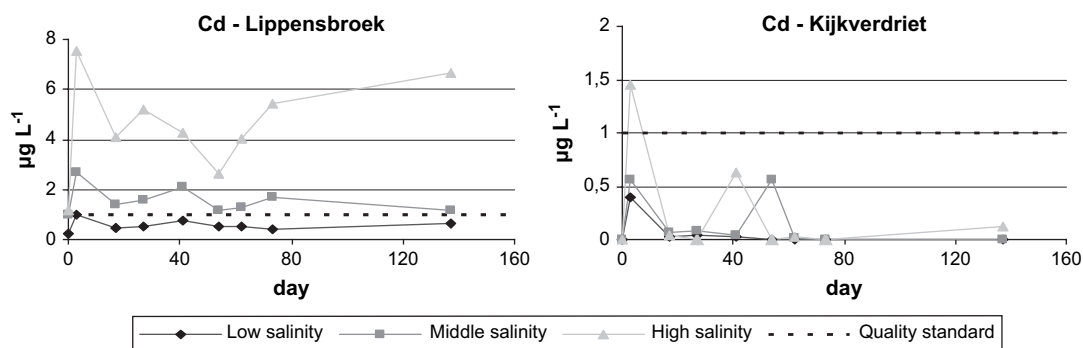


Fig. 8. Temporal variation of Cd concentrations in the surface water samples of the sediments of Lippensbroek and Kijkverdriet, flooded with water of three different salinities (low = 0.5, middle = 2.5, high = 5); quality standard represents the Flemish surface water quality standard.

reduced Kijkverdriet sediment, compared to the other, more oxidised sediments. Fe and Mn concentrations were also very high in the surface water above this sediment. They reached peak concentrations up to 78 mg L^{-1} for Fe and 29 mg L^{-1} for Mn at day 41. This might be attributed to the reduction of Fe/Mn-oxides. As a result, associated Ni might have been released, as was also already observed in the pore water. Fe and Mn concentrations however significantly decreased after day 41, which might be due to the formation of sulphides, which probably also account for the low Cd and Cu concentrations.

3.5. Metal uptake by duckweed

Not only the Cd concentration in surface and pore water, but also the uptake of metals by duckweed was affected by flood water salinity. The Cd concentrations in duckweed increased by a factor 4 when the salinity of the flood water increased from 0.5 to 5 g NaCl L^{-1} , reaching up to a maximum of $126 \text{ mg kg}^{-1} \text{ DM}$ in the Lippensbroek treatment. A highly significant Pearson correlation ($R = 0.934$) was found between Cd concentrations in the duckweed and Cd concentrations in the surface waters at day 137, just before transplanting the duckweed to the recipients. Greger et al. (1995) studied the effect of salinity on the uptake of Cd by the submerged macrophyte *Potamogeton pectinatus* from both water and sediments. Cd uptake from the water was found to decrease when increasing the salinity up to 10‰. However, in the presence of sediments, Cd uptake increased with increasing salinity. This clearly illustrates the fact that increasing salinity promotes Cd desorption from the sediment, which results in increased Cd concentrations in the water column and thus an enhanced Cd uptake by organisms. It however also promotes the formation of Cd chloride complexes in the water column, which seem to be less bio-available, especially at higher salinities. As a result, a decreasing bioavailability and toxicity of Cd with increasing salinity of the surface water was found for a series of aquatic organisms (e.g. Fischer, 1986; McLusky et al., 1986; Stronkhorst, 1993; Zanders and Rojas, 1996; Verslycke et al., 2003). Bidwell and Gorrie (2006) moreover concluded that factors such as osmotic stress, consumption of metal-contaminated sediments or metal interactions may affect metal uptake as well, next to the free ion activity.

The duckweed plants were not able to survive in the surface water above the Kijkverdriet sediment. This might be attributed to the very reduced state of this sediment, which probably accounted for the accumulation of various phytotoxins, that are by-products of sediment reduction, such as organic components, soluble sulphide species and reduced Fe and Mn (Pezeshki, 2001). The Cu and Zn concentrations in the duckweed were slightly affected by the salinity in the treatments of Lippensbroek and Galgenschoor. As the total Cu concentrations in the surface water and the pore water were not influenced by the salinity, changes in speciation of Cu might have caused an increased bio-availability without affecting the mobility. The Ni uptake by duckweed was not affected by the salinity.

4. Conclusion

Salinity primarily enhances Cd mobility. Cadmium concentrations in pore water of soils and sediments and surrounding surface waters significantly exceeded sanitation thresholds and quality standards during flooding of initially oxidized sediments. This effect was significant at salinities as low as 0.5. This implies that risks related to Cd leaching to ground water and Cd uptake by organisms are relevant when constructing flooding areas in the brackish zones. These risks can be reduced by inducing sulphide precipitation because Cd is then immobilised as sulphide and not anymore reacting to changes in salinity. This could be achieved by permanently flooding the polluted sediments, because sulphates are sufficiently available in the river water of the brackish part of the estuary. Microbial sulphate reduction is not expected to be limited by organic matter availability as biomass turnover is very high in intertidal reedbeds. Stimulation of sulphide formation should however be done with great caution as accidental oxidation of the sulphide-rich sediments could also create a significant risk for metal mobilisation, which is facilitated by increasing salinity. In that way, a “chemical time bomb” can indeed be created. Especially in the freshwater sediments and soils, low sulphate availabilities might be limiting for sulphide formation.

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