

# Factors affecting metal concentrations in the upper sediment layer of intertidal reedbeds along the river Scheldt

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Factors that play a role in determining metal accumulation in sediments of 26 intertidal marshes which are mainly vegetated by reed plants (*Phragmites australis*) were assessed along the Scheldt estuary (Belgium and The Netherlands). In the upper 20 cm sediment layer, several physico-chemical properties (clay, silt and sand content, organic matter, carbonate and chloride content, pH and conductivity) and aqua regia extractable metals (Cd, Cr, Cu, Ni, Pb, Zn) were determined. The sediments were significantly contaminated with trace metals. The Cd concentrations often exceeded the Flemish soil remediation thresholds for nature areas, whereas Cr, Cu and Zn levels indicated moderate contamination. Pb concentrations occasionally were high, whereas Ni concentrations leaned towards background values. Organic matter was the single most important predictor variable for total metal contents in regression models, except for Cr. Additional significant predictor variables were clay or chloride content, depending on the metal. Observed metal concentrations at sites within a range of a few km from specific point-sources of metals (e.g. shipyards, industrial areas with metallurgic activities, affluents, major motorways) were somewhat higher than predicted by the models, whereas they were lower than predicted at sites which are regularly subjected to flooding by water of high salinity. The ratio between observed and predicted concentrations seems to be a valuable tool for the identification of areas which are specifically impacted by point sources.

## Introduction

The river Scheldt sources in the north of France and empties into the North Sea in The Netherlands after a trajectory of about 355 kilometers.<sup>1</sup> The river is subjected to tides in the estuarine part, which extends from the mouth to the city of Ghent (Belgium), about 160 kilometers upstream. Valuable nature areas, including fresh, brackish and saltwater intertidal marshes, are situated in this part of the basin and along the tributaries. The Scheldt estuary is especially unique, as it accommodates one of the only remaining freshwater tidal zones in Europe. Moreover, the government hopes to even enhance the ecological value by creating permanent wetland conditions in a major controlled flooding area. This currently is being constructed along the river near Antwerp (Belgium), primarily to prevent flooding of inhabited areas during storm tides. Wetland conditions will be achieved by allowing the river water to flow into the flooding area during each high tide, and not only during storm tides.

The areas along the river Scheldt are densely populated and industrialized.<sup>2</sup> Approximately 7 million people live in the river basin, with urban areas near Lille (France), Ghent, Brussels and Antwerp (Belgium). The largest industrial areas are concentrated near Lille (France), Antwerp (Belgium), along the canal from Ghent to Terneuzen (Belgium), and near Vlissingen (The Netherlands). This industrial and urban development has had a considerable impact on the Scheldt estuarine environment. The surface area of the intertidal marshes has decreased and a significant part of the intertidal flats has been contaminated by heavy metals. The temporarily flooded sediments and their associated plant litter are expected to be major sinks for these metals.<sup>3</sup> Metal accumulation in the marsh sediments is determined by input coming from discharge of industrial and urban sewage or by atmospheric deposition, but also by the extent to which the substrate is capable to bind and release metals. The latter is governed by a range of factors, such as the cation exchange capacity, organic matter contents and redox conditions of the sediments and the pH and chloride contents of the interstitial water. These properties determine the nature and stability of metal species, and thus have an impact on the metal mobility, bioavailability and potential toxicity.<sup>4</sup> Disclosure of the most important factors determining the metal contamination levels of the tidal flats should help to evaluate whether and under which conditions wetland creation is a safe option, and thus contribute to a more sustainable development and management of wetland

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ecosystems. This study aimed to do so for the tidally influenced freshwater and brackish water marshes in the Scheldt estuary, which are vegetated by reed plants (*Phragmites australis*). These are primarily located between the city of Ghent (Belgium) and the Dutch–Belgian border.

Total metal concentrations in the upper 20 cm sediment layer were determined at 26 of these intertidal reed beds. The sediments were characterized for a range of physico-chemical properties including clay, silt, sand, organic matter and carbonate content of the solid fraction, and chloride content, pH and conductivity of leachates. Factors affecting the metal concentrations in this upper sediment layer were identified. Surface sediments were sampled as we aimed to focus on risks for metal accumulation in newly created wetlands, studying only the most recent depositions. Moreover, the interaction between the soil and biosphere is most obvious in this upper sediment layer.<sup>5–10</sup> The upper sediment layer on the studied marshes is alternately subjected to flooded and emerged conditions, which prevents permanently and deeply reduced conditions from being established.<sup>11</sup> The factors affecting post-depositional metal mobility within the upper 1 m sediment profile (e.g. sulfide formation) will be discussed in another paper.

## Materials and methods

### Study sites

The study was carried out in the part of the Scheldt estuary downstream the city of Ghent which is subjected to tidal influences (Fig. 1). All study sites are tidal marshes vegetated by a monospecific stand of common reed, *Phragmites australis* (Cav.) Trin. ex Steud.

### Sampling procedure

In August 2002, the upper intertidal sediment was sampled on each location. Three sediment cores (about 6 cm diameter, 20 cm long) were augered at low tide, about 5 metres from each other. They were transported to the lab in plastic bags, air-dried for three weeks and then ground in a hammer-cross beater mill (Gladiator BO 3567).



Fig. 1 Situation of the sampling sites along the tidal river Scheldt.

## Analyses

All used glassware and containers were washed in a laboratory dishwasher, subsequently soaked overnight in 5% ultrapure 65% HNO<sub>3</sub> and rinsed with deionised water. The pH was measured in a 1/5 sediment/distilled water suspension after equilibration for 18 h.<sup>12</sup> The conductivity was measured in the filtrate of a 1/5 sediment/distilled water suspension, shaken for 1/2 h.<sup>12</sup> 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<sub>2</sub>SO<sub>4</sub> added to 1 g of sediment.<sup>13</sup> Texture analyses were conducted on samples obtained by mixing equal amounts (30 g) of the three samples at each location. They were performed at the Research Institute for Nature and Forest (INBO) using laser diffraction (Coulter LS200, Miami, FL, USA) 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<sub>3</sub> and shaken for 30 min. The filtrate was titrated with 0.05 M AgNO<sub>3</sub> using potentiometric end-point detection.<sup>12</sup> Pseudo-total metal contents were determined by aqua regia extraction.<sup>14</sup> Therefore, 7.5 ml HCl and 2.5 ml HNO<sub>3</sub> were added to 1 g of sediment. The suspension was digested overnight, subsequently heated under reflux, filtered and diluted to 100 ml. The Cd, Cr, Cu, Ni, Pb and Zn concentrations in these extracts were analysed using ICP-OES (Varian Vista MPX, Varian, Palo Alto, CA, USA) and expressed on a sediment dry mass (DM) basis. A certified reference sediment of the Scheldt estuary (CRM 277) was also analysed in triplicate using the same method. Results varied from 92.5 to 101.7% of the certified aqua regia extractable values. Statistical analyses involved the calculation of Pearson correlation coefficients (*R*) between the average analyses results obtained for each parameter and sampling site, using SPSS 12.0 (2003).

## Results and discussion

### Sediment properties

Physico-chemical sediment properties are summarized in Table 1. Chloride concentrations and conductivity both generally decreased with increasing distance from the river mouth (Fig. 2). Moreover, these variables were strongly positively correlated ( $R = 0.983$ ,  $p < 0.001$ ). The influence of the salty seawater can be clearly distinguished at sampling locations up to about 75 km from the river mouth. At that point, the river water still has a significant chloride content ( $>0.5 \text{ g L}^{-1}$ ) at both low and high tides. Further from the mouth, the surface water is not affected anymore by salty seawater during high river discharges.<sup>1</sup>

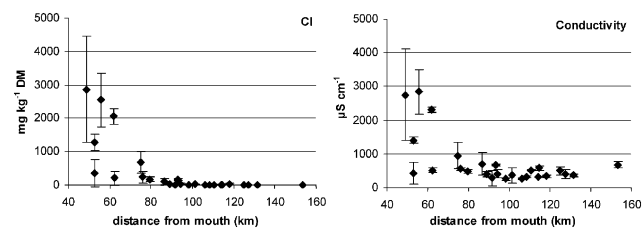
The pH of the sediments varied between 7.2 and 8.7. The high carbonate contents indicate a significant buffering capacity of these sediments against acidification. In the pH range of the sampled sediments, metal solubility is expected to be minimal. In addition to the pH effect, metals may precipitate as carbonates, which additionally explains a decreased metal availability.<sup>15</sup>

**Table 1** Summary statistics of metal concentrations and sediment properties in the upper sediment layer of 26 intertidal marshes along the river Scheldt ( $n = 78$ ; 3 samples taken at each sampling site)

	Mean	Minimum	10th percentile	Median	90th percentile	Maximum
Cd/mg kg <sup>-1</sup> DM	7.6	0.5	1.7	7.5	13.0	21.9
Cr/mg kg <sup>-1</sup> DM	134	26	45	147	195	244
Cu/mg kg <sup>-1</sup> DM	97	4	19	96	166	513
Ni/mg kg <sup>-1</sup> DM	37	8	13	38	58	71
Pb/mg kg <sup>-1</sup> DM	143	13	37	146	218	459
Zn/mg kg <sup>-1</sup> DM	595	37	132	650	868	1501
% Clay	32	5	13	35	47	48
% Silt	43	<1	18	51	59	66
% Sand	25	<1	1	9	71	95
% OM	11.6	1.1	2.9	12.2	19.9	23.3
% CaCO <sub>3</sub>	7.6	2.5	4.9	7.1	10.5	13.4
Cl/mg kg <sup>-1</sup> DM	393	<2	<2	21	1754	3993
pH	7.6	7.2	7.3	7.5	8.1	8.7
EC/μS cm <sup>-1</sup>	730	130	250	530	1790	3720

Generally, clay and silt contents increased and sand contents decreased with increasing distance from the river mouth (Fig. 3). Upstream from 106 km, all soils were characterised by high clay and silt contents. This can be attributed to natural estuarine variations in geochemistry and particle settling, which is related to the variable water velocity. Locally higher sand contents might be related to locally higher flow rates of the river water, especially at sampling sites where the river is less wide or deep. The spatial variability of suspended sediment settling within the tidal marsh (*e.g.* perpendicular to the river and marsh edge) also masks the general trend. Sandy particles are expected to settle nearest to the river, while clayey sediment particles are transported further away from the marsh edge, where the water flow rate decreases. Moreover, some sites exhibited high sand contents, which should be attributed to relatively recent infrastructure works; *e.g.* the very high sand content at 76 km from the river mouth is due to the presence of an artificially created sandy beach next to the sampling site.

The organic matter concentrations were variable, ranging from 1.6 up to 21.0%. They were significantly correlated with clay concentrations ( $R = 0.920$ ,  $p < 0.001$ ). This could be due to their similar settling characteristics, slower organic matter decomposition by limited oxygen diffusion in clayey sediments and/or adhesion of organic molecules to clayey sediments. Total metal concentrations are depicted in Fig. 4 as a function of the distance to the river mouth. Background values and remediation thresholds for upland soils in nature areas according to the Flemish environmental legislation<sup>16</sup> are also indi-



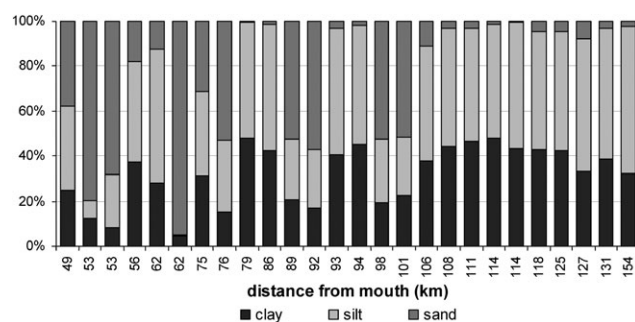
**Fig. 2** Chloride concentrations and conductivity in the upper sediment layer of 26 intertidal marshes along the river Scheldt as a function of the distance from the river mouth, error bars represent standard deviation at each sampling site ( $n = 3$ ).

cated. They are based on natural relationships between metals and organic matter and clay contents in Flemish upland soils. In that way, they are also site-specific. The Cd concentrations often exceeded the remediation values, whereas the Ni concentrations leaned towards the background values. According to the Flemish environmental legislation, the sediments should be considered as being moderately contaminated by Cr, Cu and Zn. Lead concentrations were quite high at some locations. The contamination did not reveal any clear trend as a function of the distance to the river mouth.

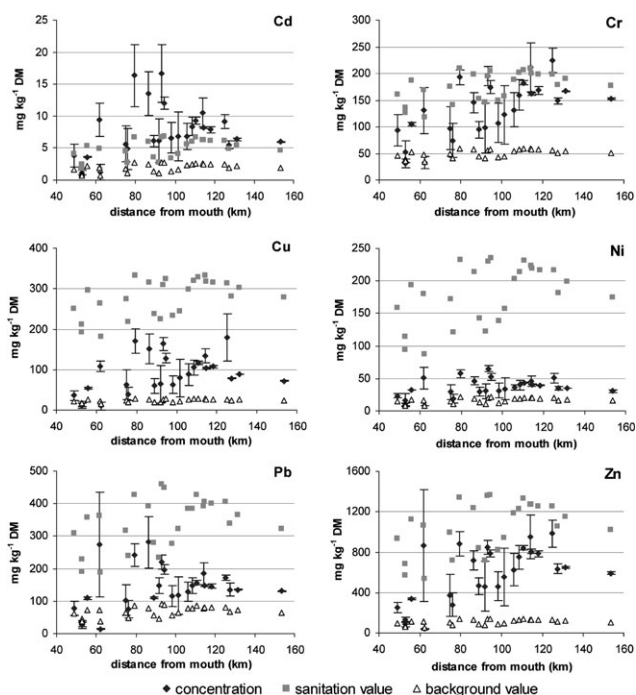
The metal concentrations could also be compared with the Flemish reference metal concentrations for river bottom sediments, according to the Flemish Environment Agency.<sup>17</sup> However, in our opinion, only little value should be attached to these reference values as they are a geometrical average of concentrations in river sediments of Flanders. They are not related to the physicochemical sediment properties, such as clay or organic matter contents.

### Origin and fate of metals in the river Scheldt

Most of the metal contamination in the upper sediment layer of intertidal flats is expected to originate from the deposition of polluted sediment particles from the adjacent surface waters. Paucot and Wollast reported very high Cd, Cr, Cu, Pb and Zn contamination levels in the water column of the Scheldt estuary in the early 90s. Particulate metal concentrations in the freshwater part of the estuary significantly



**Fig. 3** Texture of the upper sediment layer of 26 intertidal marshes along the river Scheldt as a function of the distance from the river mouth.



**Fig. 4** Total metal concentrations (diamonds) and site specific sanitation threshold levels (squares) and background values (triangles) as a function of the distance to the river mouth; error bars represent standard deviation at each sampling site ( $n = 3$ ).

exceeded the background concentrations in river waters, world averages and values for various European estuaries which are well known to be polluted.<sup>18</sup> According to Baeyens, dissolved and particulate metal concentrations in the Scheldt estuary decreased significantly in the period 1978–1995. A comparison with other estuaries classifies the Scheldt as moderately polluted for all metals in the dissolved phase, but as highly polluted in the particulate phase, especially for Cd.<sup>19</sup> Van Eck attributed the high Cd levels in the sediments to a wide range of sources. Metallurgic and ore processing industries (phosphate and fertilizer production) were characterized as point sources, whereas use of batteries, paints and plastics constitute diffuse sources. He stated that 95% of the total Cd amounts in the Western Scheldt would originate from the Sea

Scheldt section of the river. The largest input is believed to originate from industries situated near Rupelmonde and the port of Antwerp. It is estimated that they contribute for more than 75% of the total Cd emission in the Sea Scheldt.<sup>20</sup> Affluent rivers might also contribute to the metal input. Near Rupelmonde, for example, the river Rupel empties into the river Scheldt. The water of the river Rupel contains contaminants originating from *e.g.* the cities of Brussels and Mechelen as it is connected to the Brussels–Scheldt canal and the river Zenne *via* the river Dijle. The Flemish government reported that wastewater of households also significantly contributes to the surface water contamination with Cd (6.3%), Cr (21.2%), Cu (17.2%), Ni (19.3%), Pb (15.4%) and Zn (11.8% of its total input). According to the Flemish government, up to 37.7% of the Cd loads in surface waters of the Flemish region can be directly attributed to industrial activities (mainly metallurgy, chemistry, paper and cardboard industries). Industrial activities are less important sources for Cr, Cu and Ni. The use of antifouling paints at shipyards is, however, reported to contribute to an important extent to the Cu loads. Non-specific sources, such as corrosion of building materials, use of wood preservatives, atmospheric deposition, soil erosion and leaching were also significant sources for most of the metals. For Cu, Pb, Ni and Zn, significant parts of the surface water loads could not, however, be attributed to certain activities. Some sources have not yet been identified properly, such as corrosion of metals from hulls of old ships or from the anodes (mainly Zn) used to protect hulls from corrosion, metal leaching from antifouling paints, metal fluxes from ground water to surface water and the use of metal-containing pesticides by households.<sup>21</sup> Recently, increasing Cu and Zn concentrations in waters of the Blackwater Estuary (UK) were attributed to the increasing use of Cu as a replacement for Sn in antifouling preparations for boats and the use of Zn sacrificial anodes on pleasure craft.<sup>22</sup>

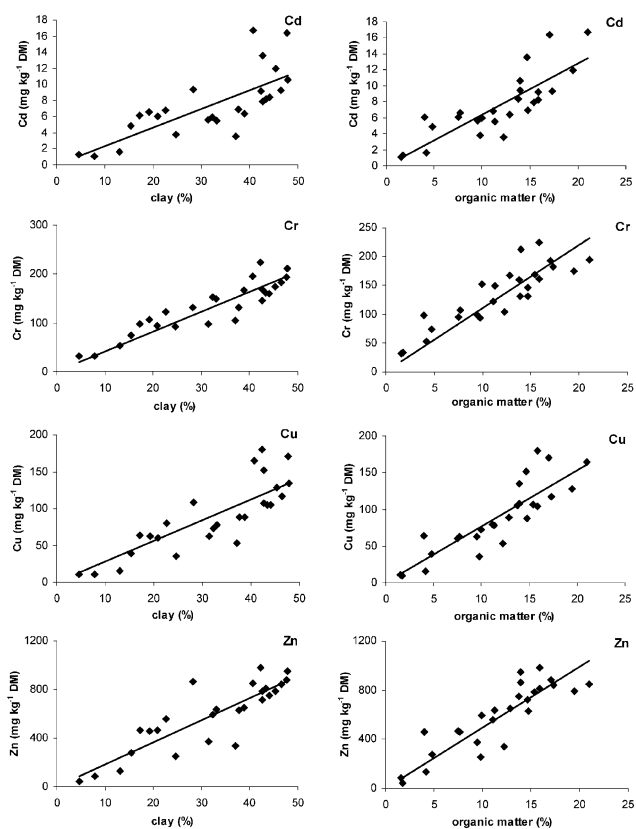
#### Factors affecting metal contents in intertidal Scheldt sediments

Pearson correlations between metal concentrations and sediment properties are presented in Table 2. Chloride concentrations or conductivities were not correlated with metal concentrations. Significant, positive correlations were, however, observed between metal concentrations and clay, silt or

**Table 2** Correlations between some sediment characteristics (pH, carbonate concentrations, conductivity, chloride concentrations, organic matter, clay, silt and sand concentrations) and metal concentrations ( $n = 26$ ) in the superficial intertidal sediment layer of the Scheldt estuary

		pH	Carbonate	Conductivity	Cl	OM	Clay	Silt	Sand
Cd	Correlation	-0.540 <sup>a</sup>	0.212	-0.230	-0.305	0.823 <sup>a</sup>	0.739 <sup>a</sup>	0.627 <sup>a</sup>	-0.699 <sup>a</sup>
	Sig.	0.004	0.299	0.258	0.130	0.000	0.000	0.001	0.000
Cr	Correlation	-0.813 <sup>a</sup>	0.063	-0.252	-0.339	0.883 <sup>a</sup>	0.910 <sup>a</sup>	0.811 <sup>a</sup>	-0.883 <sup>a</sup>
	Sig.	0.000	0.759	0.213	0.091	0.000	0.000	0.000	0.000
Cu	Correlation	-0.662 <sup>a</sup>	0.166	-0.245	-0.332	0.871 <sup>a</sup>	0.841 <sup>a</sup>	0.719 <sup>a</sup>	-0.800 <sup>a</sup>
	Sig.	0.000	0.417	0.227	0.098	0.000	0.000	0.000	0.000
Ni	Correlation	-0.658 <sup>a</sup>	0.224	-0.103	-0.188	0.920 <sup>a</sup>	0.828 <sup>a</sup>	0.746 <sup>a</sup>	-0.807 <sup>a</sup>
	Sig.	0.000	0.272	0.617	0.359	0.000	0.000	0.000	0.000
Pb	Correlation	-0.522 <sup>a</sup>	0.334	-0.031	-0.124	0.765 <sup>a</sup>	0.713 <sup>a</sup>	0.731 <sup>a</sup>	-0.749 <sup>a</sup>
	Sig.	0.006	0.095	0.880	0.547	0.000	0.000	0.000	0.000
Zn	Correlation	-0.772 <sup>a</sup>	0.153	-0.260	-0.347	0.872 <sup>a</sup>	0.866 <sup>a</sup>	0.806 <sup>a</sup>	-0.862 <sup>a</sup>
	Sig.	0.000	0.455	0.199	0.083	0.000	0.000	0.000	0.000

<sup>a</sup> Correlation is significant at the 0.01 level (2-tailed). <sup>b</sup> Correlation is significant at the 0.05 level (2-tailed).



**Fig. 5** Correlations between Cd, Cr, Cu and Zn concentrations and clay or organic matter concentrations in the superficial intertidal sediment layer of the Scheldt estuary (intercept with the  $y$ -axis was not significant and set to zero).

organic matter concentrations (e.g. Fig. 5). Generally, correlation coefficients decreased in the following order: organic matter–metal content > clay–metal content > silt–metal content. Van Eck already reported a strong association of metals with clayey particles and organic matter in the Scheldt estuary.<sup>20</sup> Other authors also found significant relationships between a number of heavy metals and organic carbon<sup>23–26</sup> and/or grain size.<sup>24,27</sup> This indicates that adsorption to clay and organic matter may play an important role in the distribution patterns of metals in wetlands. Indeed, the high within-site variability of the metal concentrations (Fig. 4) also seems to result from a high within-site variability of grain-size and organic matter concentrations.

One might expect that metals leach from the sediments with decreasing pH,<sup>28</sup> which should result in positive correlations between pH and total metal concentrations. However, these correlations were found to be negative in our study. This might be attributed to the pH fluctuating in a rather narrow range (7.2 to 8.7) because the sediments are well-buffered. Moreover, a decreased pH of intertidal Scheldt sediments seems to reflect increased acidification with increased organic matter concentrations, which results in a significant, negative correlation between organic matter concentrations and pH ( $R = -0.712$ ,  $p < 0.001$ ). This acidification might result from an increased CO<sub>2</sub> and organic acid production during the decomposition of organic matter. The negative correlations

between metal concentrations and pH, in turn, might result from the combination of the significant negative correlation between the organic matter concentration and pH on the one hand and the significant positive correlations between organic matter and metal concentrations on the other hand. Organic complexation thus affects metal accumulation to a greater extent than the pH in the well-buffered intertidal sediments of the Scheldt estuary.

When metal concentrations are plotted against clay or organic matter concentrations, some locations can be distinguished at which metal concentrations are significantly higher than expected from the correlation between clay or organic matter and metal concentrations (e.g. significantly above the regression line in Fig. 5). This may reflect that these sites are specifically influenced by point-sources of metal emission. Elevated metal concentrations at locations between 92 and 95 km from the mouth could be attributed to metals being released there into the Scheldt by an affluent which collects the wastewater originating from e.g. the city of Brussels. These sites are also located just downstream a former shipyard (at 98 km from the river mouth) where metal-based paints have been used for several decades during the construction of boats. Spencer *et al.* also reported elevated metal concentrations near shipyards of the Medway Estuary (Kent, UK).<sup>29</sup> The shipyard was, however, closed in 1994, which suggests that historically contaminated intertidal sediments at these locations are not readily replaced or covered by significant amounts of less contaminated sediments. In the freshwater zone of the estuary, elevated metal concentrations can be found at two more sites. One is situated next to an industrial area in Hoboken (86 km from the river mouth) where metallurgic activities have been located since the early 20th century. The other one is located at 79 km from the river mouth, situated also downstream this industrial area, and on the crossing of a major Belgian motorway and the ring road of the city of Antwerp. Lead, in particular, may accumulate in waters surrounded by a network of roads and bridges,<sup>25,30</sup> whereas Jones *et al.* also reported a zinc refinery to be a major source of trace-element contamination in the Derwent estuary in Tasmania. They found pollutants to be released into the estuary during bulk handling at the refinery wharf, by proximal atmospheric fall-out from bulk handling, from stockpiles or stack emissions, and/or from surface water and groundwater discharge. Contaminants were distributed downstream from the refinery by combined fluvial and tidal activity, while the latter also caused an upstream movement.<sup>31</sup>

In the brackish part of the estuary, one site can also be distinguished which is seriously contaminated, especially by Cd (9.4 mg kg<sup>-1</sup> DM), Pb (274 mg kg<sup>-1</sup> DM) and Zn (864 mg kg<sup>-1</sup> DM). It is situated at 62 km from the river mouth in the middle of the industrial areas of Antwerp harbour, with metallurgic activities nearby. Cd and Cr concentrations are, however, also very close to the remediation thresholds at several sites where the elevated levels cannot be related to specific point-sources. Yet at these sites, Cd and Cr concentrations conform to values predicted from the regression models.

Some locations exhibit metal concentrations that are significantly below these predicted by regression between metal and clay or organic matter concentrations (e.g. significantly

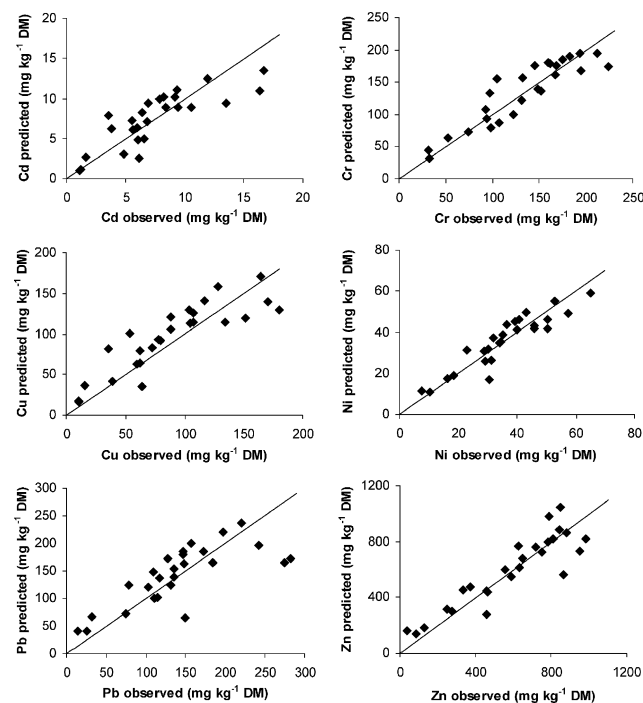
**Table 3** Results of a stepwise linear regression for metal (Cd, Cr, Cu, Ni, Pb and Zn) concentrations in superficial intertidal Scheldt sediments as a function of pH, clay, carbonate, organic matter and chloride concentrations. *R* represents the correlation coefficient and sig. *F* the significance of the overall model, whereas the *p*-values between brackets in the last column represent the significance of the individual regression coefficients (= sig. *t*)

	<i>R</i>	Sig. <i>F</i>	Regression equation
Cd	0.823	<0.001	Cd (mg kg <sup>-1</sup> DM) = 0.186 ( <i>p</i> = 0.870) + 0.627 ( <i>p</i> < 0.001) × OM (%)
Cr	0.910	<0.001	Cr (mg kg <sup>-1</sup> DM) = 17.440 ( <i>p</i> = 0.146) + 3.625 ( <i>p</i> < 0.001) × Clay (%)
Cu	0.900	<0.001	Cu (mg kg <sup>-1</sup> DM) = 4.819 ( <i>p</i> = 0.666) + 7.660 ( <i>p</i> < 0.001) × OM (%) – 13.255 ( <i>p</i> = 0.021) × Cl (g kg <sup>-1</sup> DM)
Ni	0.920	<0.001	Ni (mg kg <sup>-1</sup> DM) = 7.815 ( <i>p</i> = 0.006) + 2.414 ( <i>p</i> < 0.001) × OM (%)
Pb	0.765	<0.001	Pb (mg kg <sup>-1</sup> DM) = 26.186 ( <i>p</i> = 0.233) + 9.797 ( <i>p</i> < 0.001) × OM (%)
Zn	0.904	<0.001	Zn (mg kg <sup>-1</sup> DM) = 109.656 ( <i>p</i> = 0.089) + 43.730 ( <i>p</i> < 0.001) × OM (%) – 80.688 ( <i>p</i> = 0.013) × Cl (g kg <sup>-1</sup> DM)

below the regression line in Fig. 5). Several of these sites are situated in the higher salinity part of the estuary. This suggests the deposition of cleaner sediments originating from the sea and/or a role of salinity in metal release from the sediments. Due to increases of chloride concentrations when inland fresh river water mixes with seawater, heavy metals indeed may mobilise from the sediments as soluble chloride-complexes.<sup>32</sup> Moreover, an increase of the salinity is associated with an increase in the concentrations of major elements (Na, K, Ca, Mg), which compete with heavy metals for the sorption sites.<sup>33</sup> As a result, trace metal mobilisation is observed when estuarine sediments are brought in contact with seawater.<sup>34</sup> In our study, this was supported by a stepwise linear regression analysis that included pH, clay, carbonate, organic matter and chloride concentrations as predictor variables (Table 3). For most metals, the procedure retained organic matter as the most significant predictor variable. Thus, organic matter contents seemed to primarily affect Cd, Cu, Ni, Pb and Zn contents, whereas Cr contents were mainly determined by clay contents. Chloride concentrations were also included in the regression equation for Cu and Zn, as they still significantly (*p* < 0.05) contribute to explaining additional variability after inclusion of organic matter, although the effect of the organic matter is much more significant. The latter is confirmed by the calculation of the standardised regression coefficients (Beta-values) for both the model predicting Cu concentrations (0.843 for the organic matter and –0.226 for the chloride concentration) as for the model predicting Zn concentrations (0.842 for the organic matter and –0.241 for the chloride concentration). The regression coefficients for chlorides were negative, which indicates a decreasing trend in metal contents with increasing chloride contents. This was also the case for Cd and Cr, but chloride concentrations were not included in the regression equation, as their effect was not significant at the 0.05 level after addition of organic matter or clay as predictor variables. Chloride contents were not significant for Pb and Ni, which indicates that Pb and Ni concentrations are not affected by variations in chloride concentrations.

According to some authors, e.g. Horowitz *et al.*,<sup>27</sup> comparison of predicted with actual concentrations can be used as a screening or reconnaissance tool to preliminarily identify sites or specific trace elements requiring further evaluation. Concentrations predicted by using the above mentioned equations were therefore plotted against observed concentrations (Fig. 6). The observed/predicted ratios varied between 0.24 and 2.39. Values between 1.0 and 1.2 are indicative of elevated

metal concentrations, but could not always be related to the vicinity of point sources. In contrary, ratios above 1.2 were only found near clearly identified point sources. For most metals, the highest values were indeed found near point sources which have already been mentioned above. Unfortunately, we have not been able to accurately quantify the contributions of these individual point sources to the total elevation of metal contents. The impact of the point sources on the pollution levels at the sampling sites does not only depend on the distance between the source and the sampling site, but also on many other factors, such as the emission frequency and history of the pollution source, inundation frequency, sediment accretion rate at the sampling site, *etc.* Observed/predicted ratio's slightly above 1.2 were also found a few hundred metres upstream from a wastewater treatment plant, from which the effluent flows into the river Scheldt, and near an old shipyard at which steel cables are still being produced. The observed/predicted ratio thus seems to be a valuable tool



**Fig. 6** Relationships between metal concentrations predicted by using the equations from Table 3 and observed metal concentrations in superficial intertidal Scheldt sediments.

for the identification of areas which are specifically impacted by point sources. For the Scheldt estuary, sites bearing values above 1.2 can be considered as sites for which metal contents are significantly increased by specific point sources.

## Conclusions

The superficial intertidal sediment layer of the river Scheldt is significantly contaminated with trace metals. The Cd concentrations often exceed the Flemish remediation thresholds for nature areas, whereas the sediments are moderately contaminated by Cr, Cu and Zn. Lead concentrations are occasionally high. Nickel concentrations, however, lean towards background values. The metal concentrations were positively correlated to the organic matter and clay concentrations. Hence, a model was developed for the prediction of metal contents based on the clay or organic matter contents. However, observed metal concentrations at sites within a range of a few km from specific point-sources of metals (e.g. shipyards, industrial areas with metallurgic activities, tributaries, major motorways) were somewhat higher than predicted by that model, whereas they were lower than predicted at sites which are regularly subjected to flooding by water of high salinity. The ratio between observed and predicted concentrations seems to be a valuable tool to identify areas which are specifically impacted by point sources. For the Scheldt estuary, sites bearing values above 1.2 can obviously be considered as specifically impacted sites.

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## References

- 1 W. Baeyens, B. Van Eck, C. Lambert, R. Wollast and L. Goeyens, *Hydrobiologia*, 1998, **366**, 1–14.
- 2 J. Stronkhorst, *Neth. J. Aquat. Ecol.*, 1993, **27**, 383–393.
- 3 G. Du Laing, G. Van Ryckegem, F. M. G. Tack and M. G. Verloo, *Chemosphere*, 2006, **63**, 1815–1823.
- 4 G. Du Laing, N. Bogaert, F. M. G. Tack, M. G. Verloo and F. Hendrickx, *Sci. Total Environ.*, 2002, **289**, 71–81.
- 5 R. Swennen, J. van der Sluys, R. Hindel and A. Brusselmans, *J. Geochem. Explor.*, 1998, **62**, 67–79.
- 6 S. Dittmann, *J. Sea Res.*, 2000, **43**, 33–51.
- 7 G. Y. Miron and G. L. Desrosier, *Mar. Biol.*, 1990, **105**, 297–306.
- 8 O. A. Negrello Filho, A. J. Underwood and M. G. Chapman, *J. Exp. Mar. Biol. Ecol.*, 2006, **328**, 240–250.
- 9 A. Zipperle and K. Reise, *J. Sea Res.*, 2005, **54**, 143–150.
- 10 G. Katrak and F. L. Bird, *Mar. Freshwater Res.*, 2003, **54**, 701–708.
- 11 G. Du Laing, D. Vanthuyne, B. Vandecasteele, F. M. G. Tack and M. G. Verloo, *Environ. Pollut.*, 2007, DOI: 10.1016/j.envpol.2006.10.004.
- 12 E. Van Ranst, M. Verloo, A. Demeyer and J. M. Pauwels, *Manual for the soil chemistry and fertility laboratory*, International Training Centre for Post-Graduate Soil Scientists, University of Ghent, Gent, 1999, p. 100.
- 13 R. E. Nelson, in *Methods of Soil Analysis, Part 2. Chemical and Microbiological Properties*, ed. A. L. Page, R. H. Miller and D. R. Keeney, ASA, Madison, WI, USA, 2nd edn, 1982, pp. 181–197.
- 14 A. M. Ure, in *Heavy Metals in Soils*, ed. B. J. Alloway, Blackie and Son, Glasgow, UK, 1990, pp. 40–73.
- 15 T. Guo, R. D. DeLaune and W. H. Patrick, Jr, *Environ. Int.*, 1997, **23**, 305–316.
- 16 Vlarebo, Flemish Soil Remediation Decree ratified by the Flemish government on 22/2/1995, (translated from Dutch).
- 17 W. De Cooman and L. Detemmerman, *Water*, 2003, **6**, 1–7.
- 18 H. Paucot and R. Wollast, *Mar. Chem.*, 1997, **58**, 229–244.
- 19 W. Baeyens, *Hydrobiologia*, 1998, **366**, 157–167.
- 20 B. Van Eck, *The Schelde Atlas: an image of an estuary*, Schelde Informatie Centrum/Rijksinstituut voor Kust en Zee, Middelburg, The Netherlands, 1999, p. 120.
- 21 MIRA, Environmental Report Flanders, Background document 2005: Distribution of heavy metals, Flemish Environment Agency, 2005, (translated from Dutch).
- 22 R. H. C. Emmerson, S. B. O'Reilly-Wiese, C. L. MacLeod and J. N. Lester, *Mar. Pollut. Bull.*, 1997, **34**, 960–968.
- 23 J. C. Callaway, R. D. Delaune and W. H. Patrick, *Mar. Pollut. Bull.*, 1998, **36**, 82–96.
- 24 M. M. A. Shriadah, *Water, Air, Soil Pollut.*, 1999, **116**, 523–534.
- 25 K. A. Gallagher, A. J. Wheeler and J. D. Orford, *Biol. Environ.*, 1996, **96B**, 177–188.
- 26 T. Suzuki, K. Moriyama and Y. Kurihara, *Aquat. Bot.*, 1989, **35**, 121–127.
- 27 A. J. Horowitz, K. A. Elrick and R. P. Hooper, *Hydrol. Processes*, 1989, **3**, 347–364.
- 28 R. P. Gambrell, J. B. Wiesepepe, W. H. Patrick, Jr and M. C. Duff, *Water, Air, Soil Pollut.*, 1991, **57–58**, 359–367.
- 29 K. L. Spencer, A. B. Cundy and I. W. Croudace, *Estuarine, Coastal Shelf Sci.*, 2003, **57**, 43–54.
- 30 G. Evans, R. J. Howarth and M. A. Nombela, *Appl. Geochem.*, 2003, **18**, 973–996.
- 31 B. G. Jones, B. E. Chenhall, F. Debretson and A. C. Hutton, *Aust. J. Earth Sci.*, 2003, **50**, 653–667.
- 32 H. C. H. Hahne and W. Kroontje, *J. Environ. Qual.*, 1973, **2**, 444–450.
- 33 N. F. Y. Tam and Y. S. Wong, *Environ. Pollut.*, 1996, **94**, 283–291.
- 34 W. J. F. Standring, D. H. Oughton and B. Salbu, *Environ. Int.*, 2002, **28**, 185–195.