Investigation on trace metal speciation and distribution in the Scheldt estuary

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HIGHLIGHTS

- Trace metal (TM) speciation was assessed using DGT and active sampling techniques.
- The lability of all studied TM increases in the middle estuary.
- All studied TM are mainly bound to particles in the upper part of the estuary.
- A decrease is historically observed for particulate TM, while dissolved TM increase.
- In Europe, the Scheldt estuary remains one of the most contaminated estuaries.

GRAPHICAL ABSTRACT
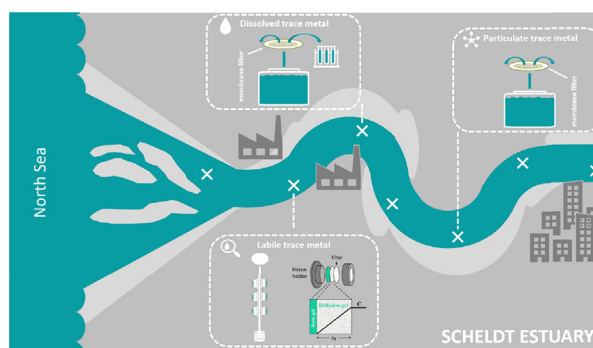
ABSTRACT

The biogeochemical behavior of Cd, Co, Cr, Cu, Ni and Pb along the historically polluted Scheldt estuary (Belgium - The Netherlands) was investigated in this study. As never studied before in this area, labile trace metals were measured using the passive sampling technique of Diffusive Gradients in Thin-films (DGT), while total dissolved and particulate trace metal concentrations were assessed using classic active sampling techniques. This dual approach allowed us to highlight the variations of trace metal speciation and distribution in the estuarine surface waters, considering environmental and physicochemical gradients along the transect. The large data set obtained was then compared with literature data of historical measurements along the Scheldt (from 1980 until now), but also from other estuaries. As emphasized by our results, trace metal mobility and partitioning along the Scheldt estuary was mainly driven by biogeochemical reactions which were strongly influenced by gradients of specific estuarine physico-chemical parameters, such as salinity, turbidity, temperature and so on. Hence, all species of trace metals displayed a non-conservative behavior. More precisely, dissolved labile fractions of trace metals showed higher levels in the middle estuary, where many solubilization and remobilization processes occurred due to turbulent mixing mechanisms and an increasing salinity. Our study confirmed the decreasing trend historically observed for particulate metals along the Scheldt, as well as the rising concentrations recorded for dissolved trace metals which might also lead to an increase of their labile fraction measured by the DGT. Finally, these preliminary results suggested that a more regular monitoring of labile metal along the Scheldt estuary is essential to have an in-depth understanding of trace metal speciation and to review bioavailability of trace metals within estuarine ecosystems.

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1. Introduction

In Europe, no fewer than 70,000 km of coastline boards marine environments. European littoral zones gather 40% of its total inhabitants and represent as well 40% of its economy (European Environment Agency, 2013), highlighting its importance as a natural resource. Estuaries often stride along these coasts and form ecotones: connecting land and ocean, freshwater and seawater (Hobbie, 2000; Meire et al., 2005). Whether they are subject to strong tide influences or not, they are highly productive systems and are homes for important biomes (Meire et al., 2005). Moreover, they play an important role in determining the future and fate of many elements transported by rivers. Historically, estuaries have been major sites for the development of strong anthropogenic activities, driven by industry, agriculture, fishery and tourism as well (European Environment Agency, 2008; Förstner and Wittmann, 2012). Discharges of chemical compounds such as trace metals (transported by rivers and tributaries, but also metal-rich effluents along estuary shores) pass, deposit and accumulate in the water column and sediments of estuaries (Förstner and Wittmann, 2012), where they eventually take various forms (free ions, labile or complexed, associated with particles, colloids, etc.) (Diop et al., 2014; Gonzalez et al., 2007; Illuminati et al., 2019). They can deposit via sedimentation and accumulate along the estuarine bed (da Silva et al., 2017). They can also enter the water column either by surface processes (atmospheric deposition, flow from rivers) or by sediment resuspension (tides, marine traffic and dredging activities), leading to the remobilization of metallic contaminants (Peres et al., 2016). Along estuaries, natural modification of physicochemical parameters (pH, turbidity, oxygen, salinity, etc.) and biological processes also influence the mobility and bioavailability of these trace metals in the estuarine ecosystem (Bianchi, 2007; Du Laing et al., 2009; Folens and Du Laing, 2017).

At the European scale, the Scheldt estuary drains a basin considered as highly industrialized and goes through major urban and harbor areas like Antwerp, Ghent (Belgium) and the Netherlands. The total Scheldt river basin forms one of the most populated and industrialized river basin in Europe (Baeyens, 1998; De Neve et al., 2020) with a very high economic activity but also an important biological value (Meire et al., 2005). Past and present wastewater discharge and historical metal pollution from industries and refineries have strongly affected the environmental quality of this coastal ecosystem (Baeyens et al., 2005; Deycard et al., 2014). Historically, many surveys endeavored to measure dissolved and particulate trace metals along the Scheldt estuary and further along the Belgian coasts (Baeyens, 1997; Baeyens et al., 1987, 1998a, 1998b, 2005; Duinker et al., 1982; Gao et al., 2013; Regnier and Wollast, 1993; Teuchies et al., 2013; etc.). However, to our knowledge, none of them attempted to report the labile contents of trace metals, yet the most bioavailable and hazardous fraction in the water column (Gao et al., 2019; Linnik et al., 2018; Simonsen et al., 2019; Tusseau-Vuillemin et al., 2007). Moreover, if dissolved and particulate trace metal levels have been indeed investigated for a long time in the Scheldt, a monitoring gap seems to appear since 2010 (due to the lack of project funding). To fulfill such lack of knowledge and to achieve an advanced understanding of trace metal speciation and distribution along the Scheldt estuary, this work assessed labile, dissolved and particulate trace metals in the surface estuarine waters. Especially since trace metal bioavailability and consequently toxicity mainly depend on their speciation rather than on their total concentration only (Aldana et al., 2018; Allen and Hansen, 1996; Landner and Reuther, 2004).

In a nutshell, this study focuses on the distribution, transport and partitioning of six trace metals (Cd, Co, Cr, Cu, Ni, Pb) in the highly urbanized Scheldt estuary. The objectives of this research are (i) to assess the metal contamination and fluxes released into the Scheldt estuary, (ii) to discuss the speciation and potential fate of these trace metals along the estuarine system, regarding various biogeochemical gradients and (iii) to project our results over a timeline from the early 80's and compare them on an European scale.

2. Material and methods

2.1. Chemicals and materials

To clean and prepare all materials including Glass, PE and Teflon bottles, Teflon and glass plates, nitric acid (HNO$_3$; Fisher, Trace Metal Grade, 65%), distilled nitric acid (HNO$_3$; Fisher, Trace Metal Grade, 65%; distilled in the laboratory), Milli Q water (Millipore) were used. For the DGT preparation, Chelex®-100 (Bio-Rad, 200–400 mesh size), cross-linker (DGT Research, Lancaster), acrylamime (40%, Merck), ammonium persulfate (APS; Merck), tetramethylethylenediamine (TEMED; Merck, >99%), DGT pistons (caps and bases, DGT research, Lancaster), 0.45 μm-pore size filter membranes (Merck Millipore, Durapore®, 0.45 μm PVDF Membrane, HVLP grade) and NaCl (Merck, Suprapur) were used. To elute the DGT resin gels, 1 M HNO$_3$ was prepared by diluting 63 mL HNO$_3$ (Fisher, Trace Metal Grade, 65%) into 937 mL Milli Q water. For sample digestion, distilled nitric acid, Milli Q water (Millipore), HCl (Fisher, Trace Metal Grade, 37%), HF (Fisher, Trace Metal Grade, 40%) and H$_3$BO$_3$ (Fisher, Trace Metal Grade, 4% w/v) were used.

2.2. Study sites

The Scheldt estuary is formed by the rivers Rhine, Meuse, and Scheldt (Wollast, 1988). It ends up in the North Sea and is one of the European estuaries where the tidal strength has the most influence (Vlaams Instituut voor de Zee, 2012). The estuary starts from the city of Vlissingen (km 0: mouth, the Netherlands) and extends to the city of Ghent (km 160: upper part, Belgium), with a mean depth of 10 m and a funnel shape (Fig. 1). It is a typical tide-dominated estuary (Scanes et al., 2017). More precisely, it exhibits an intricate morphology composed of flood- and ebb-channels, large intertidal flats and salt marshes (Meire et al., 2005). The estuarine zone is defined by water salinity (brackish to seawater) and also by significance of tidal influences. In Ghent, a series of locks limiting the tide influence are considered as the boundary of the upper-Scheldt river. The longitudinal salinity of the estuary is mostly determined by the importance of the river discharges. As the Scheldt estuary is a relatively shallow and well-mixed system, vertical salinity gradients are minor or insignificant (Soetaert et al., 2006; Van Damme et al., 2005). In this mixing zone, pollutant transport is widely controlled by the long residence time of the water masses. This entails a high stagnancy of contaminants in the water column and consequently accentuates their accumulation in sediments (de Souza Machado et al., 2016). In parallel, strong variations of biogeochemical parameters and bioavailable fractions of chemical compounds have been observed in the estuarine area (Wollast, 1988).

As previously suggested by Baeyens (1998), the Scheldt estuary can be divided in two main zones, regarding their hydrodynamical and physicochemical properties (Fig. 1). The first one goes from 1 to 10 PSU and usually shows lower salinity, high turbidity, high sedimentation and lower water oxygenation. This zone was previously called the geochemical filter, however downstream, trace metal distribution was likely to be more influenced by biological processes like phytoplankton activity and it was called the biological filter (Baeyens et al., 1998a, 1998b). The monitoring gap and this previous literature (more than 20 years ago) highlighted a need of a new monitoring survey, in order to reconsider the processes occurring in these zones nowadays. This was also one of the reasons for this monitoring project. Overall, the metallic contamination along the Scheldt has been widely influenced by large inputs of trace metals and other physicochemical factors resulting in oxygen depletion, high turbidity and high sedimentation (Baeyens et al., 1998a, 1998b).
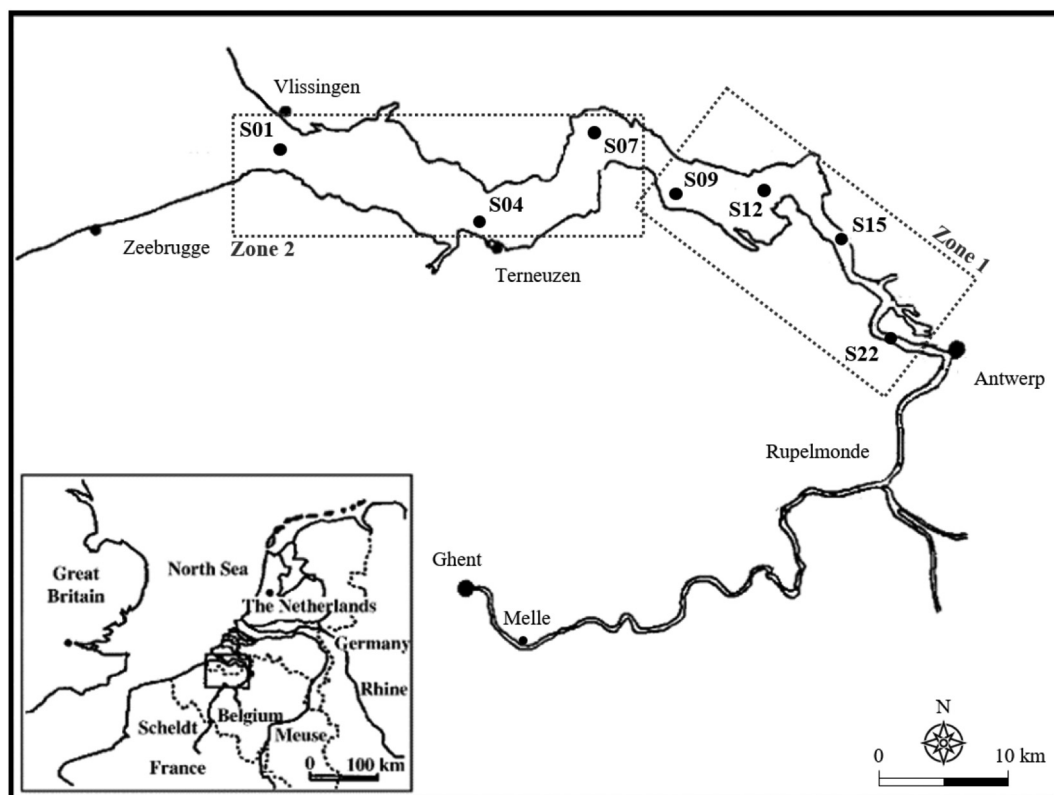
Fig. 1. Location of the sampling sites along the Scheldt estuary. Two distinct zones were defined, according to the work of Baeyens (1998).

In this study, seven stations designated as S01, S04, S07, S09, S12, S15, S22 (Fig. 1) were sampled from the city of Antwerp (Belgium) to the mouth of the Scheldt estuary in Vlissingen (The Netherlands). The sampling expedition was performed onboard of the R.V. Belgica in March 2019. Early spring constitutes a key-season in such aquatic environment and an ideal period to investigate trace metal bioavailability since the biomass (e.g. phytoplankton) expands and grows again in this period. Surface water sampling and in situ measurements were carried out from a Zodiac, in order to avoid contamination of the research vessel. Data about water tide and water flow were recorded during the sampling and is presented in Table 1.

2.3. In situ measurement of physio-chemical parameters

Temperature, pH, salinity and dissolved oxygen saturation were measured in situ at each station with a multi-meter (VWR International

Table 1
Water tide and flow during the sampling campaign along the Scheldt estuary (retrieved from Vlaamse Milieumaatschappij, Waterbouwkundig Laboratorium, Maritieme Dienstverlening & Kust en De Vlaamse Waterweg NV, internal communication).

Date	City	Tides	
		High tide	Low tide
19th March 2019	Vlissingen	00:21	06:51
		12:44	19:12
	Antwerp	02:21	09:06
		14:34	21:27
20th March 2019	Vlissingen	01:09	07:42
		13:30	19:58
	Antwerp	03:01	10:01
		15:46	10:34
		Average flow (m³ s⁻¹)	
19th - 20th March	Melle (Zeeschelde)	44.82	
March 2019	Melle (Zeeschelde)	48.30	
Year 2019	Melle (Zeeschelde)	17.94	

bvba, Multimeter MU 6100 H set 2) and using electrodes previously calibrated. To measure pH, combined glass and Ag/AgCl/KCl electrodes (VWR, pHenomenal® 111) were used; dissolved oxygen and temperature were measured using a membrane covered galvanic sensor (VWR, pHenomenal® Oxy 11-3); and salinity by a 2-pole graphite sensor (VWR, pHenomenal® Co 11). Measurements were conducted in freshwaters, brackish waters as well as in seawaters, following a salinity gradient: a correction of the pH and dissolved oxygen recordings was therefore made according to the method of Aminot and Kérouel (2004). The measurements were taken twice: at DGT deployment and once again at DGT removal (see Section 2.4.1).

2.4. Trace metal measurements

2.4.1. DGT sampling of labile metal fractions

The DGT technique relies on a controlled diffusive transport of analytes and is usually either applied in the water column (e.g. Baeyens et al., 2011; Zhang and Davison, 1995) to assess labile trace metal fractions or inserted vertically in sediments (e.g. Gao et al., 2006, 2015; Zhang et al., 2002) to determine high-resolution vertical profiles of trace element concentration and/or flux at the sediment-water interface (SWI). The DGT technique allows to assess a time integrated concentration of labile trace metal fraction, which is a good indicator of the element bioavailability in an aquatic system (Bade et al., 2012; Baeyens et al., 2018; Davison, 2016; Roig et al., 2011; Sierra et al., 2017; Simpson et al., 2012). In this study, the DGT pistons were composed of a round plastic molding (a cap and a piston base, both assembled), holding together three successive layers, which were: a membrane filter (0.45 μm pore size cellulose acetate – 0.125 mm thick), a diffusive hydrogel (polyacrylamide hydrogel – 0.8 mm thick) backed up by a resin gel (Chelex®-100 binding resin – 0.4 mm thick). The DGT samplers were deployed in the water column of each selected sampling point.

The diffusive and the resin gels were prepared according to the method reported by Zhang and Davison (1995) and the assembly of DGT probes is described in Gaulier et al. (2019). All procedures above were carried out in an analytical clean laboratory. At each sampling station, 6 DGT pistons were enclosed for ±24 h in a plastic cage which was held with a 2 m nylon rope below the water surface, anchored to the seabed using a weight and lifted to the surface with the help of a buoy. The time and temperature of DGT deployment and removal were recorded at each station and further used for DGT concentration calculations. Six procedural blanks were treated in the same way (except for the deployment step).

After deployment, labile trace metals, accumulated on the resin gel, were eluted in 1 mL of 1 M HNO_3 for at least 24 h. The eluents were then diluted five times with MQ-water, prior to their analysis. Using the mass of the accumulated metals on the resin gel, the labile metal concentration was then calculated based on the Fick's first law in a steady state, as described in Gaulier et al. (2019), assuming a perfect sink condition (i.e. all metal ions arriving at the interface between the diffusive hydrogel and the resin gel were immediately bound onto the resin).

2.4.2. Sampling of dissolved and particulate metals

At the same time the DGT pistons were deployed and retrieved, estuarine water samples were taken below the surface in two replicates, using glass bottles. Prior to use, these bottles were cleaned with 10% HNO_3, rinsed three times with Milli-Q water in the laboratory and with estuarine water in the field. 500 mL of water samples were then filtered using 0.45 µm pre-weighted filter membranes (Merck Millipore, Durapore®, HVLP grade), under a clean laminar flow hood in a clean laboratory onboard. The filtrate was acidified with 0.2% distilled HNO_3 and then stored in a clean Teflon bottle, at 4 °C. The filters were stored at −18 °C and later treated for the analysis of suspended particulate metal phase. The acidified filtrates (water samples) were finally diluted 10 times with MQ water, prior to analysis.

The filters used for the water sample filtration were dried under a laminar flow hood for 2 days and weighted again. The mass difference of the filters was recorded for the calculation of particulate metal concentrations and for the determination of the Suspended Particulate Matter (SPM) amount. The filters were digested by concentrated HF (40%), concentrated HCl (37%), concentrated HNO_3 (65%) and H_3BO_3 (4%), as described in Gaulier et al. (2019). To validate this digestion method, the certified reference material IAEA-405 (CRM; estuarine sediment, International Atomic Energy Agency) was treated in the same way as the filter samples. The results of the CRM were within the range of certified values and are displayed in the supporting information section.

2.4.3. Trace metal analysis

In all sample solutions, trace metals (Cd, Co, Cr, Cu, Ni, Pb and Al) were determined using a High Resolution Inductively Coupled Plasma Mass Spectrometer instrument (HR-ICP-MS, Thermo Finnigan Element II). The calibration was carried out with appropriate dilutions of a multi-element stock solution (Merck, ICP-MS standard XIII) and indium (1 µg L^{-1}) was used as an internal standard. The limits of detection (LOD) and the limits of quantification (LOQ) of the ICP-MS instrument and the DGT method are presented in Table 2. The relative standard deviation (RSD) was lower than 9.8% for all metal species. An additional CRM (SLRS-6; river water, National Research Council Canada) was also analyzed, the results were within the range of certified values and are displayed in the supporting information section.

3. Results

3.1. Physico-chemical parameters and SPM amount

The physicochemical parameters of all stations are presented in the Supplementary Information (SI) section. Initially, the salinity showed a typical longitudinal gradient along the estuary with a variation of 1 to 10

Table 2
Limits of detection (LOD) and limits of quantification (LOQ) of the ICP-MS instrument and the DGT method.

	Cd	Co	Cu	Cr	Ni	Pb
	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}	µg L^{-1}
ICP-MS instrument						
LOD	0,004	0,004	0,320	0,029	0,180	0,015
LOQ	0,006	0,005	0,656	0,037	0,194	0,021
DGT method						
LOD	0,006	0,003	0,051	0,0026	0,097	0,005
LOQ	0,013	0,005	0,097	0,0027	0,230	0,007

LOD = mean of blank + 3STD; LOQ = mean of blank + 10STD.

PSU in the inner area (zone 1; freshwater dominant, close to urbanized zones and to the city of Antwerp) and gradually increased seawards from 10 to 26 PSU (zone 2; seawater dominant, at the mouth).

The water temperature varied from 7.95 to 8.90 °C and displayed a reverse trend than salinity: a significant negative relationship was observed between these two parameters (correlation factor of −0.92, $p < 0.005$; see the SI for the complete correlation and associated p-value matrices). Even though it remained in a narrow range of values, the higher temperatures were found at low salinities, while colder ones appeared at the sea mouth.

Regarding dissolved oxygen, its saturation varied between 84 and 117% from the low salinity zone to the well-oxygenated seawaters. The dissolved oxygen saturation remained around 115% in the second zone. The water column oxygenation was significantly and positively correlated to the salinity along the estuary (correlation factor of 0.90, $p < 0.005$), while it was negatively correlated with the temperature (correlation factor of −0.81, $p < 0.05$). The pH varied from 7.88 to 8.05 and showed a similar longitudinal profile as that of dissolved oxygen with an increase seaward [correlation factor of 0.90 ($p < 0.01$)].

The total amount of SPM (> 0.45 µm) was 185 mg L^{-1} at station S22 (~ 1 PSU) indicating that the SPM levels at the first sampling point was consistent with the high water flow of the Scheldt river during the campaign (see Table 1), which brought more suspended materials from increasing erosion and resuspension processes. Then, it steeply decreased to 49 mg L^{-1} and remained below 75 mg L^{-1}, oscillating seaward.

3.2. Dissolved trace metal fractions

3.2.1. Total dissolved trace metals

The total dissolved trace metal concentration varied with the salinity gradient and followed different trends (Fig. 2). On one hand, total dissolved Cd showed a general increasing tendency seaward and its concentrations ranged between 0.05 µg L^{-1} and 0.15 µg L^{-1}. In zone 1, the total dissolved Cd content almost rose threefold, before stabilizing in zone 2.

Conversely, Co, Cu, Ni and Pb displayed clear decreasing trends seaward. The total dissolved concentrations of trace metals were in the range of 0.12–0.53 µg L^{-1} for Co, 1.78–4.58 µg L^{-1} for Cu, 0.44–2.77 µg L^{-1} for Ni and 0.10–0.28 µg L^{-1} for Pb. While Cu and Ni exhibited a gradual decrease in total dissolved concentrations as a function of salinity, total dissolved Co and Pb initially showed a sharp decline in the first 10 km of the estuary and then, with less intensity, they progressively decreased to the sea.

Finally, the longitudinal variations of total dissolved Cr were more variable along the transect: the concentration was quite constant (around 0.25 µg L^{-1}), except for station S04 (~ 20 PSU) where a maximum appeared (0.42 µg L^{-1}).

3.2.2. Labile trace metals

Along the estuary, the labile trace metal content also varied with the salinity gradient and followed fluctuating trends (Fig. 2). Generally, the labile concentration of Cd, Co, Cu and Ni was decreasing from the most upper estuarine station (S22) to the one (S01) close to the sea. However,
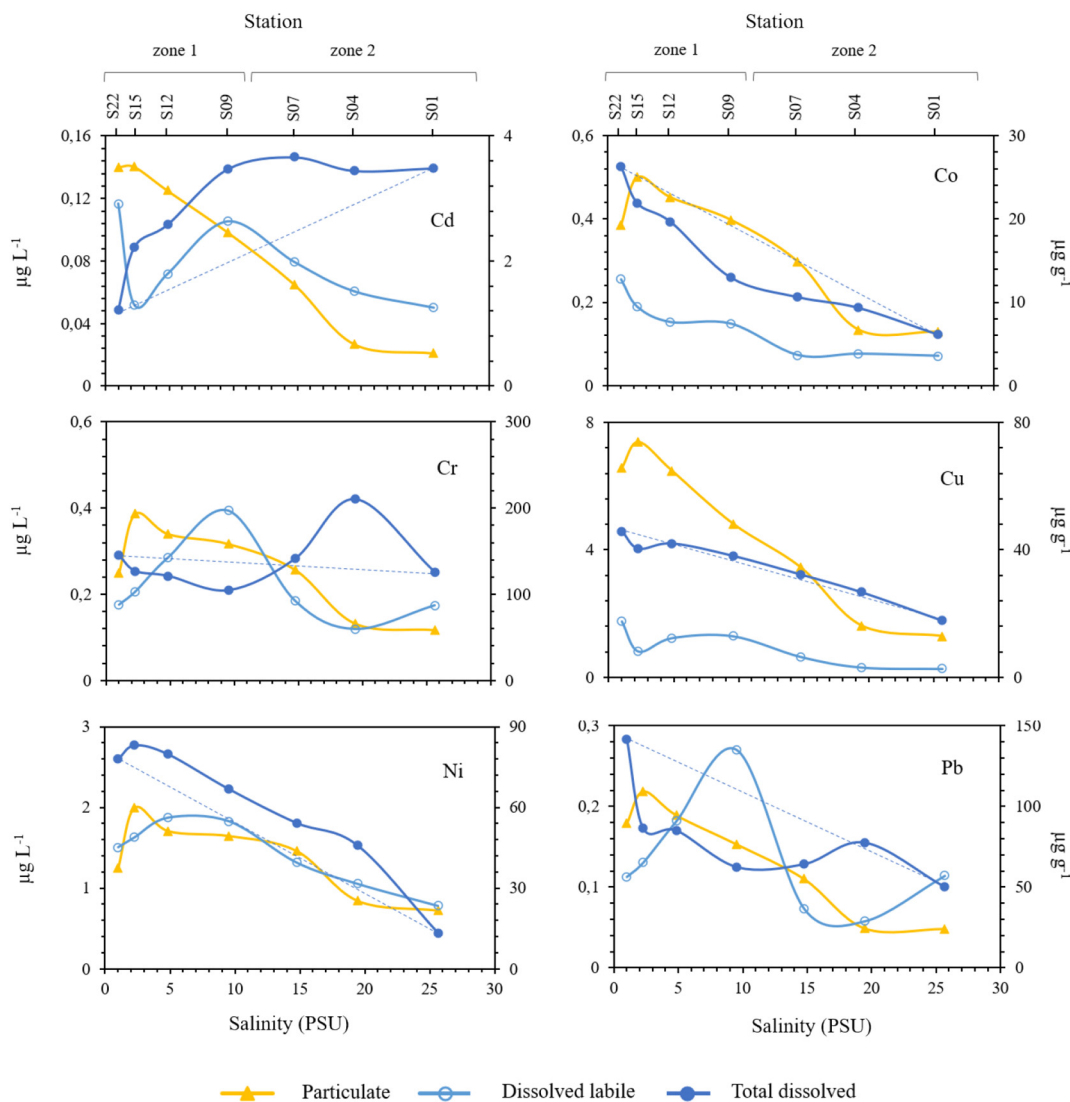
Fig. 2. Longitudinal profiles of trace metals along the Scheldt estuary waters. Particulate concentrations are given in µg g^{-1} (yellow triangles; right y-axis), total dissolved ones in µg L^{-1} (dark blue circles; left y-axis) and labile ones in µg L^{-1} (light blue circles; left y-axis). The Theoretical Dilution Line (TDL) of the total dissolved compounds is shown by the dark blue dash-line.

labile Cd and Cu started to decrease sharply by a factor 2 from station S22 to S15, before another increase until station S09 in the middle estuary. This estuarine fraction (zone 1, from S22 to S09) was the most dynamic zone, with the most fluctuations in terms of trace metal concentrations. Then, in the last kilometers to the sea, labile Cd and Cu decreased again reaching their lowest concentrations in the whole estuary.

On the other hand, the labile concentration of Cr and Pb presented oscillating curves. Labile Pb and Cr concentrations increased progressively in zone 1, until the middle estuary. This concentration peak appeared at the same point where elevations of labile Cd and Cu appeared too. Seaward, their concentration levels dropped to reach minimum values of 0.06 µg L^{-1} for Pb and of 0.12 µg L^{-1} for Cr. At station S01, their labile concentrations eventually reached similar values as at station S22 (the upper estuary).

Along the whole estuary, labile Co and Ni showed simple dilution trends with a decrease from 0.25 to 0.07 µg L^{-1} for Co, and from 1.51 to 0.78 µg L^{-1} for Ni. Both elements reached a plateau in the middle estuary, between 5 and 10 PSU, before their labile concentrations progressively decreased seaward.

Comparisons between the total dissolved concentrations of trace metals and their labile ones need to be assessed with caution, given the difference in sampling methods used for these two sub-fractions.

The labile fraction was assessed through a passive sampling technique (DGT) giving a time-weighted average concentration, while the total dissolved fraction was measured through an active sampling technique providing a "snapshot" result, at one given time, of the actual dissolved concentration.

3.3. Particulate trace metal

The particulate concentrations of trace metals in the water column presented similar profiles for all the studied elements (Fig. 2), with a clear decreasing trend from the upper estuary towards the sea. The concentrations were in the range of 3.5–0.52 µg g^{-1} for Cd, 193–59 µg g^{-1} for Cr, 25–6 µg g^{-1} for Co, 74–13 µg g^{-1} for Cu, 60–22 µg g^{-1} for Ni and 109–24 µg g^{-1} for Pb. These particulate metals initially showed a significant increase in the first 10 km of the estuary, except for Cd which remained stable in this area. Then, all of them progressively decreased to the sea, over 60 km.

3.4. Partitioning of trace metals between solid and dissolved phases

Trace metal speciation significantly changed along the estuary. Fig. 3 exhibits the longitudinal distribution of the different metal fractions.

Three trace metal pools have been considered in the water column: a la-bile fraction, a total dissolved one and a particulate fraction. Pb and Cr showed similar partitioning along the estuary: their particulate fraction accounted for more than 90% of total concentration. As the dissolved labile concentrations of Cr and Pb showed high variabilities, the comparison with the total dissolved concentrations was not relevant in this case and was therefore not included in the figure. Thus, only the total dissolved fraction is shown on Fig. 3. It had a small contribution for both elements and only showed a slight increase seaward.

Ni followed the same longitudinal pattern as Cr and Pb, yet the particulate fraction was less pronounced and the labile fraction accounted for 18 to 45% of total Ni. However, most of Co was in the particulate fraction (> 70%) and labile Co accounted for around 50% of the total dissolved Co.

Cd and Cu were two metals behaving differently in the estuary. Cd showed a clear partitioning pattern along the estuary. In zone 1 (< 10 PSU), particulate Cd was the most important fraction and accounted for ~ 72% of the total content. However, it progressively decreased seaward, handing over to total dissolved Cd. The junction between the particulate and the dissolved fraction was especially marked in the middle estuary, between station S12 and S09 (~ 5 and ~ 10 PSU, respectively).

The labile phase of Cd was dominant in the first zone and then decreased to finally be balanced, from the middle estuary to the sea.

Cu was dominated by the total dissolved fraction (accounting for around 55% of the total) which gradually increased along the salinity gradient. The labile fraction of Cu remained below 22% of the total content and below 39% of the total dissolved fraction.

4. Discussion

4.1. Environmental forces and processes along a salinity gradient

The salinity gradient allowed a division of the estuary in two zones: zone 1 (1 to 10 PSU) and zone 2 (10 to 26 PSU), and could be easily related to those defined and studied by Baeyens et al. (1998a, 1998b). Zone 1 (comprising stations S09, S12, S15 and S22) appeared as the mesohaline area, where the river discharge occurred. Zone 2 (comprising stations S01, S04 and S07) formed the polyhaline area of the estuary. According to Baeyens et al. (1998a, 1998b), zone 1 often has the most variable SPM concentrations in a one-year cycle due to a variety of sources involved but also due to the seasonal change. In March 2019, the Scheldt estuary was likely in flood (Table 1). This indicates that
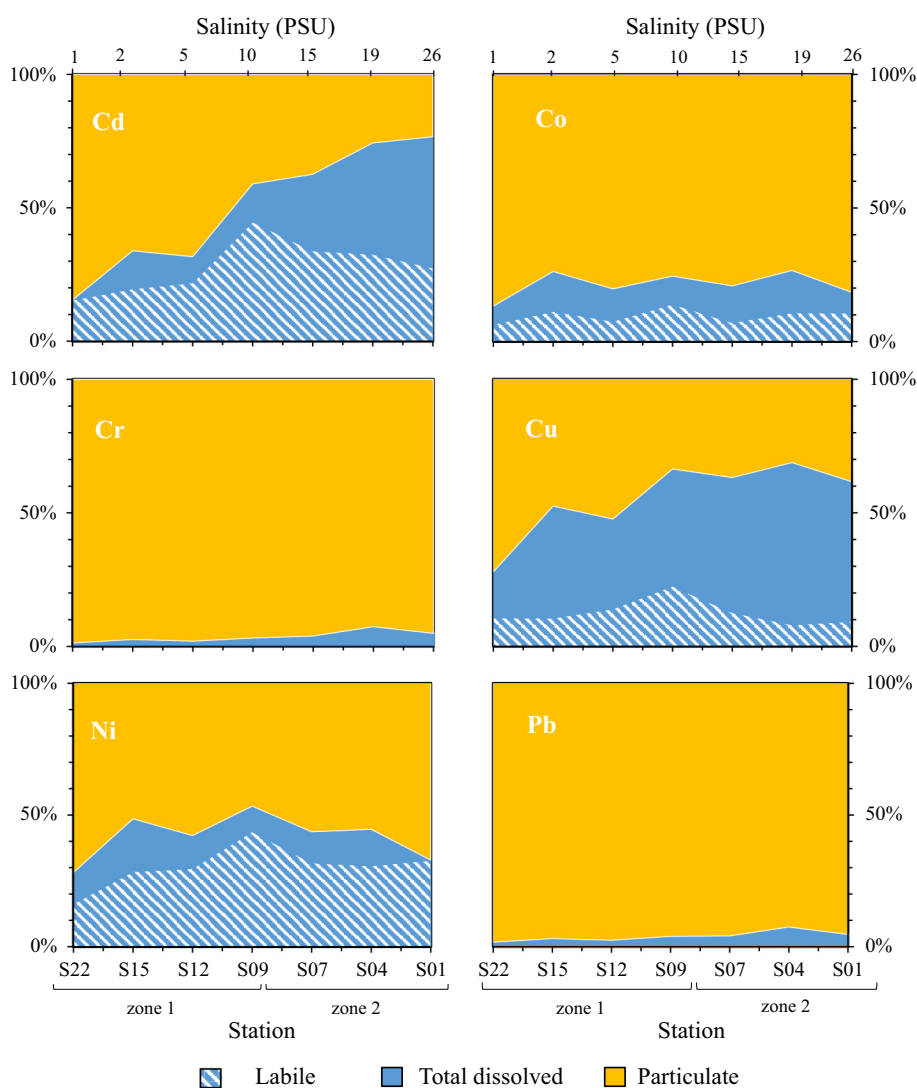

Fig. 3. Longitudinal profiles of trace metal speciation along the Scheldt estuary waters. The total metal load in the water column is illustrated by the 100% value. The particulate fraction is depicted in yellow (the particulate fraction is converted to μg L^{-1} taking into account the SPM concentration in the water column), the total dissolved fraction is depicted in blue and the dissolved labile elements (free ions or weak dissolved complexes, dynamic form measurable with the DGT passive samplers) is given in striped light blue. For Cr and Pb, only the total dissolved fraction is depicted.

the freshwater discharge and forces might had a greater influence on the upper part of the estuary during the sampling campaign, coonfirmed by the reduced salinity in zone 1 and by the higher SPM content at station S22 (see the SI). The river discharge influence was clearly observed at station S22 because the temperature and the SPM amounts in this station were high, while the available oxygen and the pH were lower than in the rest of the estuary. This state remained quite short, as a steep decrease of SPM amount occurred, because SPM were rapidly reduced and/or quickly settled down to the bottom. This type of flocculation is usually generated by an increase of salinity, which balances the negatively charged surface of freshwater particles (i.e. Van der Waals forces; Sholkovitz, 1978). Further on, dissolved oxygen, pH, and SPM slightly increased, due to various mixing forces between freshwater and seawater. Higher SPM concentrations at stations S04, S12 and S22 were linked to higher disturbance of the estuarine bed due the occurrence of stronger mixing zones and additional water discharges for S04 and S12, and with an amplified erosion of the upstream banks for S22. The elevated amount of carbonate compounds brought by the increasing salinity resulted in a pH rise seaward (de Souza Machado et al., 2016).

Ultimately, the obvious salinity gradient is one of the first typical aspects of an estuary and is the root of various physicochemical changes and processes, including a non-conservative behavior of trace metals (de Souza Machado et al., 2016; Drexler et al., 2003), as observed in this study (Figs. 2 and 3). By changing the water density and physicochemical properties (dissolved oxygen, pH, SPM, etc.), the salinity influenced trace element mobilization, availability and potential toxicity (Du Laing et al., 2008; Iglesias et al., 2020; Valenta et al., 1986).

4.2. Trace metal speciation along the Scheldt estuary

4.2.1. Influence of estuarine features on trace metal speciation

The river discharge was the main driver for metal speciation in the estuary. Thus, in the first zone (< 10 PSU), turbidity and SPM amount were high, and the particulate fraction of trace metals was the highest of the whole transect. More specifically, the maximum turbidity was observed at station S22, where high amount of SPM and metal complexes were found, flowing from surrounding rivers, bottom sediments and usually accentuated by physical forces such as tides, mixing forces, etc. (Hobbie, 2000; Robert et al., 2004). This resulted in higher trace metal adsorption and precipitation on particles (i.e. effect of the ionic strength which neutralizes colloids) (Baeyens, 1998; Gonzalez et al., 2007), explaining the highest particulate trace metal concentrations measured at this station. Further along the estuary, higher ionic strength and the presence of anions and cations tended to desorb the trace elements from particles. Thus, the metal contamination mainly came from the upper streams and rivers and a combination of particulate dilution and mixing with less contaminated downstream water made the metal concentrations in suspended particles decreased when the salinity was higher than 2 PSU.

The trace metals of interest in this study were not only influenced by a conservative dilution mechanism in the surface waters of the Scheldt estuary, but the non-conservative pattern for all the elements (to less extent for Cu and Ni, after station S15) implied a removal of these elements during the estuarine mixing, via flocculation and sedimentation processes. The longitudinal profiles (Fig. 2) suggest that these biogeochemical mechanisms were particularly important in zone 1. Dissolved Cu and Ni were less affected by such mechanisms than others and showed a near-conservative behavior, even unreactive. This is linked with a privileged complexation of Cu and Ni by organic matter enhancing their biogeochemical stability in such system, which is described and discussed further. However, this could imply higher residence time in the estuary water column and later in the sea, compared to other elements which could be easily trapped in the sediment (Turner et al., 1998).

At station S12 (~ 5 PSU), a slight local maximum of particulate metal fractions suggested a potential addition of these elements in the environment, via other riverine inputs or sediment resuspension (Fig. 2). As there was no water discharge here and given the increase of SPM in this area, the remobilization of particles from sediments (at this station and from tidal flats located around) would be the main reason (de Souza Machado et al., 2016; Teuchies et al., 2013).

At the end of the transect (i.e. close to the sea mouth), Co, Cu and Ni showed stabilizing particulate concentrations, while their total dissolved concentrations keep decreasing. In this area where the estuary is strongly influenced by the sea fluxes, marine phytoplankton may have played a role in trace metal mobilization: a biological uptake could lead to a transfer of Co, Cu and Ni from the dissolved pool to the particulate one (Paquin et al., 2003). This hypothesis could also be supported by the fact that marine phytoplankton (mostly diatoms) only thrive until the limit with brackish waters and usually show a first spring bloom at the end of March, i.e. when the sampling was done. Freshwater phytoplankton normally appear much later in summer (Naithani et al., 2016).

The evolution of labile trace metals along the estuary seemed more variable: several fluctuations appeared along the transect, including a peak at 10 PSU for all elements (Fig. 2). This mid-estuary peak was co-registered with the appearance of a strong mixing-zone (between zone 1 and zone 2). This has been interpreted as the desorption of labile elements by particles, which were locally and tidally resuspended into the water column (Martino et al., 2004; Baeyens et al., 1998a, 1998b). Several labile metals (Cd, Co and Ni) constituted a non-negligible fraction of the total dissolved pool all along the estuary. One explanation could be large riverine inputs of labile elements due to high river flow (Chester, 1990), coupled with the release from decomposing organic matter in the benthic zone (Braungardt et al., 2011; Waeles et al., 2009) and from dissolved humic substances (Balch and Guéguen, 2015; Mangal et al., 2016). Overall, the bioavailability of trace metals seemed to fluctuate significantly in the estuary, given the variations of labile concentrations. Therefore, organisms might be subject to different degrees of exposure if they move along the estuarine zones (Iglesias et al., 2020; Vicente-Martorell et al., 2009) and especially, station S09 and S22 often showed the highest labile concentrations.

The constant increase of total dissolved Cd fraction along the estuary (Fig. 3) was mainly linked to its desorption from SPM due to the increasing salinity. Cd indeed tends to form stable and dissolved complexes with chloride and sulfate (Bingham et al., 1984; Lefèvre et al., 2009), but also with low-molecular-weight organic ligands (Waeles et al., 2008). Thus, the estuarine water column was enriched in dissolved Cd mainly stemming from upstream particles. In a seaward direction, the contribution of labile Cd became less and less dominant in contrast to zone 1. Thus, the formation of labile chloro- and/or sulfato-complexes might be more pronounced until a salinity of 10 PSU, as labile species were more present upstream. While dissolved Cd organic complexes (bigger than DGT measurable species) were formed later along the estuary (zone 2), resulting from SPM desorption (Waeles et al., 2005). The same speciation pattern was also observed earlier in the Scheldt estuary by Baeyens et al. (1998a, 1998b), elsewhere in the Po river plume by Illuminati et al. (2019) and in the Venice lagoon by Morabito et al. (2018). As suggested by Illuminati et al. (2019), the colloidal Cd forming in zone 2 (after 10 PSU) to the sea might result from the adsorption and/or uptake of Cd on/in nanoplanktons (small algal cells like Coccolithophorids or Dinoflagellates) or with phytoplankton exudates. Such association could be enhanced by high concentrations of calcium in the water (Perfus-Barbeoch et al., 2002).

As observed for Cd, a continuous solubilization of Cu was noticed as well, from the upper estuary to its mouth, given the increase of its total dissolved fraction. However, the contribution of labile Cu towards the total dissolved fraction was lower than what was observed with Cd. Therefore, the dissolved Cu species were strongly bound to dissolved organic ligands, reducing the amount of free Cu ions which can

accumulate on the DGT samplers. The strong complexation of Cu with dissolved organic matter also limited the process of biosorption by organisms, in contrast with Cd (see above). The same observations were obtained by Zitoun (2019) in New-Zealand estuaries and by Ndungu et al. (2005) in the bay of San Francisco. Both studies revealed that labile Cu accounted for less than 3% of the total dissolved Cu and highlighted the role of dissolved organic compounds in regulating Cu speciation.

In the Scheldt estuarine waters, Cr and Pb speciation was undoubtedly dominated by their particulate fractions. They were not heavily affected by desorption processes and kept their particle-reactive character all along the estuary (Illuminati et al., 2019; Santschi et al., 1980; Schulz-Baldes et al., 1983). The high daily discharge at the time of sampling (Table 1) could explained the higher contribution of the particulate fraction over the area, and also the intense sedimentation in the upper estuary. Regarding the dissolved pool of Cr and Pb, their labile concentrations (indicative of bioavailability) seemed highly variable (Fig. 2). Both elements only showed a slight increase of their total dissolved fraction towards the sea. Indeed, with an increasing salinity, free ions like Ca^{2+} and Na^{2+} may have feebly replaced bound trace elements from particles as demonstrated by Fairbrother et al. (2007). The distribution of Pb between the particulate and the dissolved pools was in agreement with previous studies (Braungardt et al., 2011; Illuminati et al., 2019). Regarding Cr, Cr(III) might be the most represented one along the estuary given its affinity to the particulate pool in aquatic environments (Gustafsson et al., 2014; Pađan et al., 2019). Thus, the dissolved pool might be mainly composed of stable dissolved Cr(VI) oxo-complexes, as investigated by Pađan et al. (2019) in the Krka estuary (Croatia).

Co and Ni were little influenced by sorption processes, even unreactive to estuarine mixing because both elements only showed very small variations of their distribution along the transect. The contribution of particulate Co was slightly more important than particulate Ni. In the dissolved fractions, labile Ni was dominant while it is less pronounced for Co. In a study carried out in English estuaries, Turner et al. (1998) and Martino et al. (2004) have also shown a low biogeochemical reactivity of Ni in the estuarine waters, emphasized by its low particle-affinity and by the presence of specific dissolved organic ligands.

4.2.2. Identification of critical zones

As no reference value for labile metal fractions yet exists, our labile metal concentrations were compared with Environmental Quality Standards (EQS) for total dissolved trace metals in seawater (Directive 2000/60/CE and 2008/105/CE; Maycock et al., 2011). In this condition, labile levels were all below the EQS-yearly average values (EQS-YA). In the same way, they were all below the Acute Water Quality Criteria (WQC; Durán and Beiras, 2013), except labile Cu whose concentrations at stations S09, S12 and S22 exceeded the recommended probabilistic value of 1.39 µg L^{-1}. Dissolved concentrations of all studied metals were also below the EQS-yearly average values (EQS-YA). However, the dissolved Cd concentration at S07 was close to its EQS-YA value of 0.2 µg L^{-1}. In addition, they were all below the WQC, except for dissolved Cu exceeding the recommended probabilistic value of 1.39 µg L^{-1} at all stations. To get a better insight into the toxicity degree of the measured labile and dissolved concentrations, the results of Cd, Cu, Ni and Pb were also compared to Predicted No-Effect Concentrations (PNEC) proposed by Källqvist (2007). Our concentrations for labile and dissolved Pb were all below the PNEC of 2.49 µg L^{-1}, whatever the sampling point. The concentrations obtained for Cd remained rather close to the PNEC value of 0.18 µg L^{-1}, especially at stations S22 and S09 (for labile Cd) and from the mid-estuary (S09) to the sea (for dissolved Cd), but did not exceed it. However, the dissolved concentrations of Cu (as well as labile, except at station S01 and S04) exceeded the PNEC defined for Cu (0.64 µg L^{-1}). In the same way, dissolved concentrations measured for Ni at all stations (except S01, the closest to the sea) and labile ones at S09, S12 and S15 were higher than the PNEC proposed by Källqvist (2007; 1.53 µg L^{-1}).

Particulate Cd, Co (except the values found at station S04 and S01), Cr, Cu (except the values found at station S01), Ni and Pb (except the values found at station S04 and S01) were above the pedogeochemical references defined in this region (Sterckeman et al., 2007). In order to link the concentrations of trace metals measured in SPM to the actual contamination level of SPM, an enrichment factor (EF) of suspended particles was calculated for each element, following the calculation method of Remeikaitė-Nikienė et al., 2018. The EF values were ranked into five categories ranging from low (EF < 2) to extremely high enrichment (EF > 40) (Barbieri, 2016). EF values of Co, Cu, Cr and Ni were ≤2, which is equivalent to a minimal enrichment (Fig. 4). Upstream (between station S22 and S12), Cd showed the highest EF (in the range of 20–30) and Pb the second highest EF (close to 10). From S09 (~ 10 PSU) to the sea, the EF of Pb decreased to a moderate level, but Cd still showed a significant enrichment.

In terms of contamination, the most critical areas are located in the upper part of the estuary where the highest concentrations and enrichments were found: this was especially true for Cd and Pb, yet they are considered as substances of priority concern by the OSPAR Convention (OSPAR, 2002, 2009). SPM were much less enriched in trace metals in the direction of the sea, but, at the same time, a large quantity of SPM was also lost at the beginning of the estuary towards the estuarine bed, due to sedimentation. The dissolved pool seemed less worrying than the particulate one, but specific attention needs to be made on dissolved Cd (station S07) and Cu (at all stations) for future monitoring
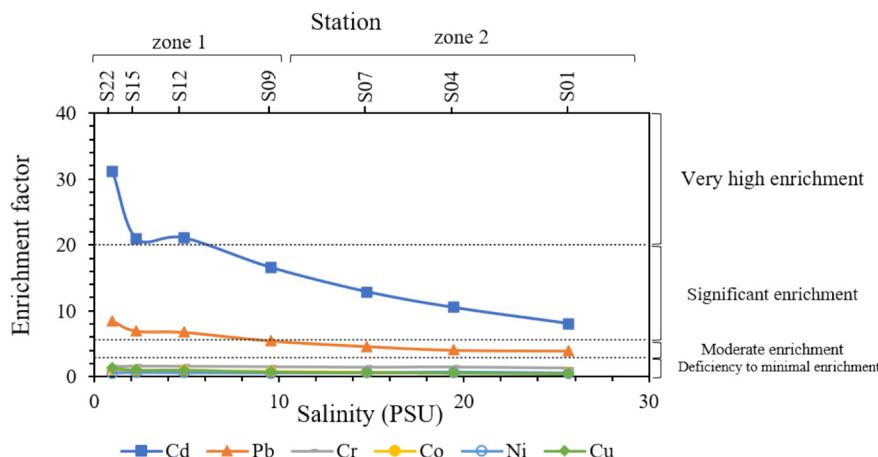

Fig. 4. Enrichment factors of particulate trace metals, along the Scheldt estuary.

surveys. Concerns are nowadays rising around the increasing use of copper-based antifouling paints on boats because they might increase the release of dissolved Cu into the aquatic environment (Matthiessen et al., 1999; Warnken et al., 1999; Elskens et al., 2014; Lagerström et al., 2020). However, a direct impact of Cu on the estuarine ecosystem could not be fully confirmed, as an important fraction of dissolved Cu eventually remained non-labile (i.e. less accessible to organisms) and was strongly bound to dissolved organic matter.

4.3. Temporal and spatial evolution of the Scheldt estuary in Europe

4.3.1. Temporal evolution of the Scheldt estuary

To answer the growing scientific and public concern about pollution status in aquatic environments, European environmental policies and regulations have settled on different directives regarding trace metal levels in water (Water Framework Directive, Marine Strategy Framework Directive; European Parliament and of the Council, 2000). In comparison with the research previously done by Baeyens et al. (1998a, 1998b) (Table 3), the total dissolved and particulate concentrations of Cd, Cu, Ni and Pb in the present study followed the same trends as those recorded in the 80's and in the 90's in the Scheldt estuary. However, particulate trace metal concentrations in the Scheldt estuary have largely decreased between 1978 and 1988 following the implementation of regulation policies regarding atmospheric emissions and direct wastewater discharges and kept on decreasing until 2010 with less intensities as highlighted by Gao et al. (2013). Our results of particulate Cd, Cu and Pb were in good agreement with this decreasing trend, at the fluvial and marine endmembers but also in the middle estuary. In the same study, Gao et al. have simultaneously shown that total dissolved trace metal concentrations in the Scheldt tend to increase from 1990 on, highlighting a shift from the particulate to the dissolved

phase for Cd, Cu and Pb. Our measurements were also in line with this observation. Along the same lines, the logarithm of the partition coefficient K_D was calculated (Gaulier et al., 2019) and compared with those of previous studies in the Scheldt (Table 3): the average K_D ranking obtained in this study was in good agreement with the past measurements, i.e. Cr > Pb > Co > Ni > Cd > Cu. Overall, Cr and Pb clearly showed a higher affinity for the particulate phase than the other elements, while Cu was the most soluble element. In this study, all the K_D values were lower than those obtained in the last decades, except for Ni due to the insufficient data in previous work. This difference was even higher in the fluvial and marine endmembers than in the middle estuary. Moreover, the K_D decrease seemed stronger for Cd and Cu than for Pb. This demonstrated the lesser affinity of Cd, Cu and Pb for the particulate phase over time, and might increase the concern around dissolved harmful fractions in the Scheldt estuary (Baeyens et al., 2005; Gao et al., 2013).

The clear decline of K_D of these trace metals becomes worrying regarding aquatic organisms which therefore have an easier access to dissolved metal species. If considering an alternative "labile" K_D using labile concentrations of trace metals instead of total dissolved ones, the average K_D ranking would be slightly different in the Scheldt estuary, i.e. Cr > Pb > Co > Cu > Ni > Cd. In this new pattern, Cd and Ni showed more concern than the other elements, as they tended to be more bioavailable, while Cr and Pb were less worrying as shown with the "classic" K_D.

The recent implementation (2006) of a wastewater treatment system in Brussels and Antwerp (Belgium) urban areas has widely changed the Scheldt water composition and therefore influenced the dissolved oxygen concentration and the speciation of trace elements (Meire et al., 2005). Thus, a different composition of particles linked with a higher amount of dissolved organic complexes could be an explanation

Table 3
Evolution of the dissolved and particulate metal concentrations in the Scheldt estuary, from 1978 until 2019 (no former data was found on Cr and Co measurements).

	Year	Cd			Cu			Ni			Pb			References
		Flu.	Mid.	Mar.	Flu.	Mid.	Mar.	Flu.	Mid.	Mar.	Flu.	Mid.	Mar.	
Dissolved µg L⁻¹	1978	0.06		0.12										Duinker et al., 1982
	1981–1983	0.09		0.07	1.0		1.1				0.23		0.18	Baeyens et al., 1998a, 1998b
	1987–1988	0.02		0.05	1.0		1.0							Zwolsman and Van Eck, 1993
	1991–1994	0.02		0.07	1.6		1.0							Paucot and Wollast, 1997
	1995	0.02		0.05	0.7		0.7				0.17		0.05	Baeyens et al., 1998a, 1998b
	1995–1997		0.07	0.04		2.3	0.9					0.14	0.13	Gao et al., 2013
	1995–1998	0.02	0.05	0.03	1.3	1.0	0.8	4.7	4.9	1.0	0.26	0.47	0.10	Baeyens et al., 2005
	2009–2010		0.21	0.06		3.0	1.7					0.14	0.11	Gao et al., 2013
	2010	0.05		0.09	2.2		1.2				0.27		0.10	Gao et al., 2013
	2019	0.05	0.10	0.14	4.6	4.2	1.8	2.6	2.7	0.4	0.28	0.17	0.10	This study
Particulate mg kg⁻¹	1978	45.0		5.0										Duinker et al., 1982
	1979	52.0			271						334			Salomons et al., 1981
	1981–1983	27.9		1.8	278		31				288		83	Baeyens et al., 1998a, 1998b
	1987–1988	12.2		1.2	213		29				207		63	Zwolsman and van Eck, 1993
	1991–1994	8.3		1.3	159		32							Paucot and Wollast, 1997
	1995	8.8		0.8	112		17				214		45	Baeyens et al., 1998a, 1998b
	1995–1997		5.1	0.8		73	20					118	49	Gao et al., 2013
	1995–1998	7.2	6.4	0.9	104	100	20	40	35	23	166	149	44	Baeyens et al., 2005
	2009–2010		3.5	0.5		65	19					85	41	Gao et al., 2013
	2010	4.3		0.5	77		15				120		28	Gao et al., 2013
	2010–2011	3.4	2.1	<LOD	58	46	24	27	22	20	105	72	39	Van Ael et al., 2017
	2019	3.5	3.1	0.5	66	65	13	37	51	22	89	95	24	This study
Log K_D	1978	5.91		4.62										Duinker et al., 1982
	1981–1983	5.51		4.41	5.44		4.45				6.10		5.66	Baeyens et al., 1998a, 1998b
	1987–1988	5.79		4.38	5.35		4.48							Zwolsman and van Eck, 1993
	1991–1994	5.64		4.30	5.01		4.49							Paucot and Wollast, 1997
	1995	5.64		4.24	5.22		4.38				6.10		5.95	Baeyens et al., 1998a, 1998b
	1995–1997		4.86	4.31		4.50	4.36					5.93	5.58	Gao et al., 2013
	1995–1998	5.68	5.11	4.42	4.92	5.00	4.38	3.93	3.85	4.37	5.81	5.50	5.66	Baeyens et al., 2005
	2009–2010		4.22	3.92		4.34	4.06					5.78	5.57	Gao et al., 2013
	2010	4.93		3.75	4.54		4.10				5.65		5.45	Gao et al., 2013
	2019	4.85	4.49	3.55	4.16	4.19	3.86	4.15	4.28	4.70	5.50	5.75	5.38	This study
Log K_D "labile"	2019	4.48	4.64	4.02	4.57	4.72	4.68	4.39	4.44	4.44	5.90	5.72	5.33	This study

Flu. (Fluvial) = S22; Mid. (Middle) = S12; Mar. (Marine) = S01.

for the change in affinity of trace metals regarding the dissolved or particulate phase (Gao et al., 2013). At a larger scale, the switch from particulate to dissolved phases could be indirectly linked to a global acidification of marine environments. But even if the decline of pH estimated or observed in the North Atlantic Ocean or in the North Sea (Blackford and Gilbert, 2007; Lauvset and Gruber, 2014; Ríos et al., 2015; Vázquez-Rodríguez et al., 2012 - for instance, −0.1 pH units since pre-industrial times in the North Sea) could match relatively well with the increase of dissolved trace metals, it is hard to predict how significant this relation is or will be in the Scheldt estuary, and how acidification may disturb interactions and processes of marine biogeochemical cycles (Blackford and Gilbert, 2007). For future monitoring, it is suggested that pH should be systematically measured during sampling for speciation studies.

4.3.2. Spatial comparison of the Scheldt estuary in Europe

The concentrations of the three metal species (particulate, total dissolved and labile) were compared to literature data of the Belgian Coastal Zone (BCZ; where the Scheldt estuary flows) and of different estuarine systems in Europe (Table 4). Both dissolved and particulate values in the BCZ were in the same order of magnitude as those measured in this study (Gaulier et al., 2019). More precisely, they were similar to the results found at the estuary mouth (station S01, ~ 26 PSU). The only exception was the concentration of particulate Cu which was higher in harbors of the BCZ than in the estuary, most likely due to an intense traffics in harbors coupled with the use of copper-based antifouling paints for boat (Gaulier et al., 2019; Jones and Bolam, 2007). Furthermore, labile trace metals in the Scheldt estuary showed two- or three-times higher concentrations than those found in the BCZ. Regarding their speciation, dissolved Cd, Cu and Ni (except for offshore stations) were the dominant species in both systems, while particulate Pb was the main issue (Gaulier et al., 2019). Same speciation patterns have been observed in previous studies in the same areas (Baeyens et al., 1987). Yet, the surroundings have changed a lot since 1987 when the latter study was performed (more inhabitants, different human activities but also different regulations regarding emissions and discharges of pollutants, new wastewater treatment system, etc.). This eventually indicated that the nature and composition of water inputs might have evolved with time, but the general speciation pattern remained most likely the same.

Within the dissolved fraction, non-labile Cd was the dominant species in the BCZ, which fits with the increase of the non-labile Cd in the estuary, seaward. Finally, Co showed the same speciation pattern in the Scheldt estuary as in Zeebrugge industrial harbor, 10 km away from the Scheldt estuary mouth (Gaulier et al., 2019). The concentrations of dissolved Cd, Cu and Pb in the Atlantic Ocean (Aparicio-González et al., 2012) were all lower than those in Scheldt estuary.

Moreover, the average dissolved Cd and Pb concentrations were higher than those measured in most European estuaries (Table 4), yet they were similar to those in the Arno, the Ebro and the Seine estuaries. Dissolved concentrations of Cu and Ni were in good agreement with those described in the same table (from 0.4 to 5.0 µg L^{-1} on average for Cu, 1.32 µg L^{-1} measured in Acheloos for Ni). Only the Severn estuary (UK) showed higher dissolved values for Cd, Cu and Pb at least (0.11–0.40 µg L^{-1}, 4.0–5.0 µg L^{-1} and 0.39 µg L^{-1}, respectively). Particulate Cd, Cu, Ni and Pb were all higher in the Scheldt estuary than in other European estuaries of France, Italy, Croatia and Greece. Compared to most of the estuaries depicted in Table 4, the Scheldt estuary shows a higher population density, as well as more industrial and agricultural activities around its shore: this could easily explain the higher concentrations of trace metals observed.

In a nutshell, the level of trace metals measured in the BCZ showed a good link with the Scheldt estuary content. The latter seemed to be more contaminated for dissolved and particulate Cd, particulate Cu and particulate Ni than other estuaries in Europe. But the Severn estuary showed either comparable or higher concentrations of trace metals than in the Scheldt estuary because it drains a heavily industrialized and urbanized mining region.

Research surveys attempting to measure labile concentrations of trace elements in estuaries are few, even though the labile fraction of metals should be a good indicator of their bioavailability. In order to overcome this issue, our results were compared to several measurements of trace metals accumulated in various organisms along the Scheldt estuary. For most of them, the sampling locations of the selected measurements were similar to the ones in this study. Thus, a comparison was made between metal concentrations in biota and labile metal concentrations at the same location. For instance, the labile

Table 4
Overview of trace metal concentrations around the Scheldt estuary's mouth and along various estuaries in Europe.

Site	Labile (L; µg L^{-1}), dissolved (D; µg L^{-1}) and particulate (P; µg L^{-1}) concentrations						References
	Cd	Co	Cr	Cu	Ni	Pb	
Scheldt estuary	0.05–0.12 (L), 0.05–0.15 (D), 0.04–0.64 (P)	0.07–0.25 (L), 0.12–0.53 (D), 0.52–3.44 (P)	0.12–0.39 (L), 0.21–0.42 (D), 4.9–21.9 (P)	0.27–1.76 (L), 1.78–4.58 (D), 1.1–11.8 (P)	0.78–1.87 (L), 0.44–2.77 (D), 1.6–6.6 (P)	0.06–0.27 (L), 0.10–0.28 (D), 1.9–16.1 (P)	This study
Belgian Coastal Zone	0.02 (L), 0.12 (D), 0.03 (P)	0.08 (L), 0.14 (D), 0.21 (P)	0.04 (L)	0.24 (L), 1.44 (D), 2.28 (P)	0.43 (L), 0.98 (D), 0.68 (P)	0.04 (L), 0.12 (D), 1.0 (P)	Gaulier et al., 2019
Atlantic Ocean	0.01 (D)			0.1 (D)		0.02 (D)	Aparicio-González et al., 2012
European estuaries							
Severn, UK	0.11–0.40 (D)			4.0–5.0 (D)		0.39 (D)	Harper, 1991
Tay, UK	0.01 (D)			0.8 (D)		0.13 (D)	Owens and Balls, 1997
Aber Wrac'h, FR	0.04 (D), 0.01 (P)			0.4–0.6 (D), 0.29 (P)			L'Her Roux et al., 1998
Gironde, FR	0.004–0.09 (D)			0.1–1.3 (D)			Michel et al., 2000
Huveaunne, FR	0.01 (D)			1.7 (D)		0.13 (D)	Oursel et al., 2013
Jarret, FR	0.01 (D)			1.8 (D)		0.08 (D)	Oursel et al., 2013
Loire, FR	0.01–0.03 (D)			0.5–1.3 (D)			Waeles et al., 2004
Rhône, FR				2.1 (D)		0.07 (D)	Ollivier et al., 2011
Seine, FR	0.03–0.20 (D)			0.76–2.29 (D)			Chiffoleau et al., 1994
Ebro, SP	0.12 (D)			1.0 (D)		0.16 (D)	Dorten et al., 1991
Marche estuaries, IT	0.01–0.020 (D), 0.01–0.02 (P)			0.4–1.97 (D), 0.1–1.0 (P)		0.07–0.15 (D), 0.03–1.86 (P)	Annibaldi et al., 2015
Arno, IT	0.1 (D)			1.7 (D)		0.2 (D)	Dorten et al., 1991
Krka, CR	0.002 (D), 0.001 (P)			0.28 (D), 0.39 (P)		0.01 (D), 0.02 (P)	Cindrić et al., 2015
Acheloos, GR				0.68 (D), 0.31 (P)	1.32 (D), 2.76 (P)	0.23 (D), 0.25 (P)	Dassenakis et al., 1997

concentrations of Cd and Ni in this study showed similar trends as their concentrations in shrimp muscle and shore crab hepatopancreas reported by Van Ael et al. (2017). The same was also observed for Pb in Oligochaeta and in European flounder gills. Cr and Cd in shrimp hepatopancreas and, to a lesser extent Cu, were also in good agreement with our data. In De Wolf et al. (2000), Cd, Ni and Pb concentrations in soft body parts and shells of the periwinkle *Littorina littorea* showed the same peak as the labile concentrations measured in this study (at ~ 10 PSU). Finally, Co and Cd concentrations in *Mytilus edulis* (Wepener et al., 2008) followed the same trend along the Scheldt estuary as their labile levels assessed in this study.

5. Conclusion

The biogeochemical behavior of Cd, Co, Cr, Cu, Ni and Pb was studied along the strongly urbanized Scheldt estuary. For the first time in this area, labile trace metal concentrations were measured in-situ using the DGT passive sampling technique, giving an insight into their bioavailability towards the estuarine ecosystem. The dissolved and particulate trace metal concentrations were assessed using classic active sampling techniques. This highlighted the variations of trace metal speciation and their partitioning coefficients in the estuarine surface waters, considering environmental and physicochemical gradients. Despite their high ecological values, estuaries are constantly changing environments, which greatly influence biogeochemical cycles of trace metals including their availability towards estuarine living organisms. In the Scheldt estuary, dissolved trace metals showed a nonconservative behavior due to the influence of various environmental gradients, such as salinity, dissolved oxygen content, etc. and due to local mechanisms, such as sediment resuspension, runoffs along the shore, etc. Moreover, different zones could be drawn, based on trace metal concentrations and partitioning and on physicochemical processes of adsorption/desorption. Thus, all metals eventually displayed an increase in their lability in the mid-estuary zone, while they were mainly bound to particles when entering the estuary. Metals like Co, Cr, Ni and Pb mainly remained under an unreactive particulate form, while others like Cd, Cu underwent several desorption and solubilization processes throughout the whole estuary. Furthermore, from the SPM amount and particulate metal concentrations, it was supposed that the sediment constituted an important reservoir for metal compounds in the upper part of the estuary, while it could also be an additional source further along the Scheldt, where the salinity increased and fluctuated.

The comparison with literature data allowed to redraw the continuum of trace metals from the Scheldt estuary to the North Sea and even further, highlighting the importance of the estuary as a major source of material. In Europe, the Scheldt estuary remained one of the most contaminated inlets: Cd, Cu and Ni being the most concerning elements. Moreover, its trace metal loads have widely and interestingly evolved from the 80's until today: showing decreasing particulate trace metal concentrations, while the dissolved ones tended to rise. Such pattern will also require an extensive monitoring in the years to come. If the input of dissolved organic matter keeps rising due to the new wastewater treatment plant, it might lead to an increase of the labile metal concentrations, which could be a major concern in a near future. Indeed, the higher the labile fraction, the more the element is bioavailable and the larger the threat for the marine ecosystem (Baeyens et al., 2018; Simpson et al., 2012). Thus, future research should focus more on the monitoring of this labile phase and on its correlation with changing conditions such as tidal cycles, rising temperatures and seawater levels, or changes in estuarine water circulation.

CRediT authorship contribution statement

Camille Gaulier: Methodology, Software, Validation, Field sampling and analysis, Investigation, Writing. **Chunyang Zhou:** Field

sampling, Analysis, Visualization. **Yue Gao:** Supervision, Writing, Data analysis, reviewing & editing. **Wei Guo:** Experimental design, Field sampling and analysis. **Marek Reichstädter:** Data treatment, Investigation. **Tianhui Maa:** Filed sampling and writing. **Willy Baeyens:** Supervision, Experimental design. **Gabriel Billon:** Investigation, supervision and visualization.

Declaration of competing interest

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

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.143827.

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