

High-resolution profiles of trace metals in the pore waters of riverine sediment assessed by DET and DGT

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Abstract

The techniques of DET (diffusive equilibrium in thin films) and DGT (diffusive gradients in thin films) were applied to obtain high-resolution vertical profiles of trace metals in freshwater sediments. In the framework of the EU-Interreg project Stardust (<http://www.vliz.be/projects/stardust/>) between France and Belgium, in which the mobility of sediment bound metals is investigated, sediment samples were collected from the Upper Scheldt River (at Helkijn, Belgium) and the Leie River (at Warneton, located at the Belgian–French border). Intra- and inter-laboratory comparisons of the gel techniques were carried out between the two laboratories involved. In general, a good agreement was observed, taking sediment heterogeneity into account. At both stations, metal pore water profiles show more or less similar tendencies although the sediment at Warneton was more anoxic than at Helkijn. A strong correlation between Fe and Co was found at Helkijn as well as at Warneton. The metal gradients at the water/sediment interface were calculated from the high resolution profiles and the conventional, low resolution profiles. Significant differences were observed.

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1. Introduction

The river Scheldt (L'Escaut in France) is a lowland-river, which takes its rise in the northern part of France (St. Quentin), and flows into the North Sea near Vlissingen (The Netherlands). The total catchment area is 22×10^3 km². The total length of the river is 355 km, the fall over the total river length is at most 100 m and the mean depth of the Scheldt Estuary is about 10

m. The river Leie (La Lys in France) is the major tributary of the river Scheldt in Flanders. It rises in the hills of Artois in France and flows NE to Gent forming the border between Belgium and France for 24 km. The pollution of the Scheldt Estuary (about 90 km long) has been studied into detail (Baeyens, 1998), but that of the upper river is not so well documented. In northern France, important metallurgical non-ferrous plants such as Metaleurop and Umicore are located along the river Deule, a major tributary of the upper Leie. High loads of numerous metals are discharged into the Deule, ranking this river as one of the most contaminated in Europe

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regarding water and sediment quality (Bourg et al., 1989). Part of this pollution is transported further downstream subsequently contaminating the river Leie and the Scheldt. In addition, the textile industry in southern Belgium (the area around Kortrijk) enhances the contamination level of the river Leie. Regarding heavy metals, the upper river Scheldt has a better water quality compared to the river Leie. The Spierre Canal (Canal de l'Espierre in France) connecting the river Leie (in France) to the Upper Scheldt (in Belgium) is a major contributor to the pollution level of the upper Scheldt River (see database of VMM, www.vmm.be). Going downstream, small factories (painting, dyes, metallurgy, and so on) also contribute to a further decrease of the water quality of the river.

The important historical discharges of metals in the upper Scheldt and Leie rivers also lead to elevated levels in the bottom sediments. Due to the surface water characteristics, especially the low levels of dissolved oxygen, an important fraction of the metals are safely stored in the anoxic bottom sediments as stable metal sulfide species. However, European regulations, such as for example the water directive (Water Framework Directive 2000/60/EC), force the Member States to comply with the new water quality standards. Therefore, wastewater treatment plants are actually built or are yet operational improving progressively the water quality. We must be aware, however, that a sudden release of the metal burden from the sediments can be triggered by any modification, even seemingly insignificant, of the sediment environment (such as variation in pH or an increased supply of oxygen from the water column as a result of actual measures for waste water treatment or as a consequence of dredging). This phenomenon is called the sediment “time bomb” by geochemists studying contaminated anoxic sediments.

Actually we are not able to predict the amount of trace metals that could be released from the sediments of the upper Scheldt and Leie rivers, as a consequence of abrupt changes in pH or redox. Therefore, understanding the behavior of trace metals (mobilization and transport) in those sediments becomes urgent. Because in a natural system trace metals can exist in a variety of species (differentiation can be carried out according to oxidation state, labile or non-labile bound to a ligand, colloid or dissolved, etc.), it is critical to know the distribution between these species as well as the processes controlling them. To study those complex processes in the river Scheldt and Leie sediments, the laboratories of Lille and Brussels universities joined forces. In strong anoxic estuarine sediments, where sulphate reducing bacteria are active, the heavy metals

are trapped as poorly soluble metal complexes whereas in other sediment types (oxic or sub-oxic) metals tend to be redissolved due to the oxidation of organic matter or due to the reduction of particulate Fe and Mn oxyhydroxides (Panutrakul and Baeyens, 1991). Normally in an organic-rich area, Pb appears to be more associated with aluminosilicates and excess-Fe and Mn-phases, while Cu and Zn are generally correlated with organic matter (Dehairs et al., 1985). The degradation of freshly deposited organic matter controls in fact the distribution of Pb, Cu and Zn in bottom sediments.

The previous studies were all carried out with conventional techniques: trace metals in sediments were assessed after slicing the sediment core and centrifugation or squeezing of the slices, achieving a relatively low spatial resolution (>1 cm). Either for centrifugation or squeezing, sectioning sediment cores should be carried out in a plastic glove-bag which during operation is kept oxygen free, by means of high purity nitrogen gas. With these techniques, artifacts could be created because even a short contact with a limited amount of oxygen can disturb significantly the original species distribution. Fe^{2+} is very sensitive to oxidation and will then precipitate. In addition, the profiles given by these conventional techniques have a common limitation especially at the surface of the sediments because the spatial resolution (typically 1 cm) is insufficient for studying geochemical processes.

Since the recent development of DET and DGT techniques (Davison et al., 1991; Davison and Zhang, 1994), high-resolution vertical profiles of metals in sediment pore waters can be assessed. With the DET technique, pore water concentration in sediment can be assessed directly (Davison et al., 1991). DET compares with the technique of dialysis peepers (vertical disposed set of dialysis cells, but instead of putting a solution in the compartments, it uses a gel that equilibrates much faster). According to Davison et al. (1991), equilibration for a typical dialysis cell (1 cm deep) and a DET gel (1 mm thick) would take 3 days and 42 minutes, respectively. According to Haper et al. (1997), equilibration for a dialysis cell (6 mm) and a DET gel (0.4 mm thick) would take 36 hours and 18 minutes, respectively. The DGT technique, based on mass transport control of the species of interest from natural water (Zhang et al., 1998a,b; Dahllqvist et al., 2002), soils (Zhang et al., 1998a,b; Harper et al., 1998) and sediment pore waters (Zhang et al., 2002; Fones et al., 2004), makes use of two hydrogel layers. A polyacrylamide gel is used as the diffusive layer, but it is backed up with a second thin film gel layer containing generally a chelex cation-exchange resin selective for trace metals. The diffusive

layer is placed in the DGT probe on top of the binding phase and covered with a membrane ($0.45 \mu\text{m}$). DGT does not directly measure the concentration of metals in bulk pore water, C_b , but rather the mean concentration, C_s , at the surface of the probe during deployment (Fones et al., 2004). The relationship between C_s and C_b depends upon the re-supply of the metal from the solid phase to solution. A full explanation of the relationship is given in Zhang et al. (2001), Harper et al. (1998) and Davison et al. (2000). Due to the structure of the DGT probe, this technique will measure only dissolved species with molecular sizes sufficiently smaller than the pore size of the hydrogel to allow them to diffuse freely through it, and which are sufficiently labile to bind on the resin's functional groups. Normally, the Chelex-100 resin is used, because the functional group, iminodiacetic acid, competes effectively with natural ligands for divalent and trivalent metal ions. However, alternative resins are described, such as the synthetic ferrihydrite resin for phosphates (Zhang et al., 1998a,b), AG50W-X cation-exchange resin for radioactive Cs and Sr (Chang et al., 1998) and the Spheron–Thiol resin for mercury (Docekalova and Decekalova, 2004; Divis et al., 2005).

In this study, in the framework of the EU-Interreg project Stardust (<http://www.vliz.be/projects/stardust/>)

between France and Belgium, DET and DGT systems have been deployed in sediment pore waters of trans-boundary rivers in Northern France (Nord Pas de Calais) and Western Belgium (West-Flanders) area (see Fig. 1) for the determination of vertical high-resolution metal profiles. The results are compared to those obtained by classical techniques, which are less effective in terms of resolution, but can be applied as a kind of control.

2. Materials and methods

2.1. Sampling area

Fine grain, muddy sediments were found at the sites of Warneton (river Leie, at the Belgian–French border), which is at the junction of an old natural river's stretch (navigation free) and a canalized part (used for navigation) and at Helkijn station, located in Belgium on the river Scheldt (Fig. 1).

Samples were collected from a shallow flat close to the riverside. Plexiglas tubes and rubber stoppers were used for collection. The cores were retrieved by hand allowing 15 cm overlying water to remain above the sediment. Sampling was performed by research groups of both the Vrije Universiteit Brussels (VUB) and the Université des Science et Technologie de Lille (USTL).



Fig. 1. Sampling stations.

Sediment cores were collected for 1) the application of DET and DGT techniques, 2) pH and redox measurements and 3) the analysis of major ions, nutrients, alkalinity and trace metals in pore waters using the conventional sectioning and centrifugation technique. The DET and DGT techniques were then applied by both groups on their respective cores, allowing an inter-laboratory comparison. Samples were collected always a few meters away from each other.

2.2. Measurement of redox potential and pH

Field measurements of redox potential and pH performed on one of the tubes, which had pre-drilled holes at 1-cm intervals, covered with tape during collection of the sediments. Electrodes were inserted in the holes to measure redox potential and pH. Measurements were realized with a combination platinum electrode (Mettler Toledo/Pt4800) and measurements of pH were realized with a combination glass electrode (Mettler Toledo/Pt4800) made especially for abrasive and hard medium. For both electrodes, the reference electrode is Ag/AgCl, [KCl]=3 M.

2.3. DET probe preparation

The procedure is similar to that of Zhang et al. (1995). A gel containing 1.5% agarose was prepared by its dissolving in an appropriate volume of 80 °C warm Milli-Q water. The mixture was placed in a boiling water bath, covered and gently stirred until all the agarose was dissolved and the solution was immediately pipetted into a preheated gel-casting probe and left to cool down to its gelling temperature (36 °C or below). The constrained DET probe's material was obtained from DGT Research Ltd. The size of the DET probes was 180 mm × 40 mm, with a window of 150 mm × 18 mm open to the aquatic system. After the gels were set, they were covered with a 0.45- μ m cellulose acetate filter (Millipore). Finally the window plate was put on top of the probe and all the elements gently pressed together. Before deployment of the DET probes, they were stored in Milli-Q water.

2.4. DGT probe preparation

Diffusive gel and resin gel were prepared as described by Zhang et al. (1995). The DGT probes (DGT Research Ltd.) were 180 mm × 40 mm in size, with a window of 150 mm × 18 mm open to the aquatic system. The resin gel was covered by diffusive gel and a 0.45- μ m pore size cellulose acetate filter. The front

window plate gently pressed the various layers together. The probes were stored at 4 °C in a closed plastic bag containing 1 ml 0.01 M trace metal free NaCl solution (5–10 g Chelex-100 were added for removing trace metals).

2.5. The deployment of handling of DET and DGT probes

Before deployment, the entire DET gel assemblies were de-oxygenated by immersing them for 24 h in a container filled with Milli-Q water and bubbling with nitrogen, whereas DGT probes were deoxygenated for 24 h in a container filled with metal free (using Chelex-100) NaCl (0.1%) solution. After sampling, the cores to be used for deployment of the DET and the DGT were immediately taken back to the laboratory. Deployment was performed at laboratory temperature at 20 °C ± 0.5 °C during 24 h. A couple of DET and DGT probes, arranged back to back, was inserted into one core. The interface of water and sediment was marked when the probes were retrieved from the sediment core.

In the laboratory all the manipulation of the gels were carried out in a laminar flow hood located in a clean room. The DET gels (typically 20 μ l) were transferred into preweighed 2-ml tubes, weighed and eluted in 1 ml 1 N HNO₃. They were generally not further diluted for analysis. The DGT probes were opened, the filter and diffusive gel were removed and the resin gel was cut into 5-mm intervals using a Plexiglas gel cutter. Each gel slice was eluted in 1 ml 1 N HNO₃ for 24 h and further diluted to 10 ml for analysis by ICPMS.

Blank DET and DGT went through all previous described steps including casting, probe construction, and deoxygenation except for the deployment step. They were treated in the same way as the sample probes. The DGT probe was sliced into 32 intervals of 5 mm; 10 slices were randomly chosen for analysis. For the DET probe, 10 of 75 blank slices were randomly chosen for analysis.

2.6. Conventional sampling and centrifugation

All handling including sample sectioning and filtration was carried out inside a nitrogen flushed glove-bag. The cores collected with conventional presectioned core samplers were cut after removing each time the plastic cover, and put in the centrifuge vessels. The samples were then sealed in order to prevent oxidation. Then they were centrifuged for 30 min at 2500 rpm. To eliminate residual small size particles, the obtained pore water was further filtered

through a 0.45- μm cellulose acetate disposable filter, collected in a clean polyethylene tube and acidified with 1% HNO_3 .

2.7. Analysis

A high-resolution inductively coupled mass spectrometry (HR-ICPMS) (Thermo Finnigan Element II) was used to determine the concentrations of the elements As, Cd, Co, Cu, Fe, Mn, Ni, Pb and Zn by VUB. USTL used a Thermo Elemental X7 Series ICPMS for the determination of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn. Fe and major elements were determined by a Varian VistaPro ICP–AES (USTL) and a Thermo Optek Iris ICP–AES (VUB).

Metals in the solid sediment phase were determined by HR-ICPMS (Thermo Finnigan Element II) after aqua regia digestion in a microwave oven (CEM Mars 5).

NO_3^- , SO_4^{2-} , Cl^- , F^- were determined by ion chromatography (DIONEX DX 500) using an anionic column AS11. NO_3^- , NO_2^- , NH_4^+ , PO_4^{3-} were also determined with classic colorimetric techniques.

Alkalinity was measured by potentiometric micro-titration on a 1-ml sample using an automatic titrator (Metrohm, Titrino 736GP).

3. Results

3.1. Ion balances in the pore waters of Helkijn and Warneton sampling stations

In sediment pore waters of Helkijn and Warneton sampling stations, all major cations and anions were determined after conventional sectioning of the core and centrifugation of the slices (see Materials and methods). The sum of all major cation concentration should match that of the anion concentration. The goodness of fit of the ion balance is an indication of the quality of analysis. In addition, for modeling the trace metal behavior in sediments, the major ion concentrations are necessary. At four different depths, ion balances were calculated (Table 1a–b). The concentrations of carbonate and bicarbonate were derived from the total alkalinity, the pH, the temperature and the thermodynamic stability constants involved in the various equilibria of the carbonate system.

The sum of positive ion concentrations (mM) = $3 * (\text{Al}^{3+}) + 2 * (\text{Ca}^{2+}) + 2 * (\text{Fe}^{2+}) + 2 * (\text{Mg}^{2+}) + 2 * (\text{Mn}^{2+}) + 2 * (\text{Zn}^{2+}) + 2 * (\text{Sr}^{2+}) + 4 * (\text{Si}^{4+}) + (\text{Na}^+) + (\text{K}^+) + (\text{NH}_4^+)$. The sum of negative ion concentrations (mM) = $2 * (\text{HPO}_4^{2-}) + 2 * (\text{SO}_4^{2-}) + 2 * (\text{CO}_3^{2-}) + (\text{NO}_3^-) + (\text{Cl}^-) + (\text{F}^-) + (\text{HCO}_3^-)$. The ionic balance was very good at Warneton

Table 1

Ion balances at (a) Warneton and (b) Helkijn calculated from the concentrations of positive and negative ions

Depth (cm)	Concentration of positive ions (mM)	Concentration of negative ions (mM)
<i>(a) Warneton</i>		
–1	16.1	16.5
–5	15.8	15.2
–9	17.6	19.2
–17	25.5	25.9
<i>(b) Helkijn</i>		
–3	8.9	11.1
–7	8.4	10.1
–11	9.0	10.9
–15	9.2	11.4

(differences are less than 10%), somewhat less good at Helkijn with a largest difference of 20%.

3.2. Comparison between blanks from DET and DGT gels and in situ concentration ranges measured with those gels

Blanks for DET gels (VUB and USTL) are shown in Table 2. Comparing those blanks with metal concentration ranges observed in the sediment cores at Helkijn and Warneton stations, it appears that the concentrations of some elements are sometimes lower than the blanks.

Blanks for DGT gels (VUB) and (USTL) are also shown in Table 2. Blanks were calculated using a deployment time of 24 h. The concentration ranges observed with the DGT gels at Helkijn and Warneton stations were only for the lowest Ni and Zn concentrations at the limit of quantification.

3.3. Laboratory comparisons

3.3.1. Intra-laboratory comparison (VUB)

In order to validate the DET and DGT techniques, two couples of DET and DGT probes arranged back to back were inserted into two sediment cores from Warneton which had been sampled close to each other. The statistical method Pearson's Product Moment Correlation was used to test the correlation between the two DET probes. Iron, manganese and cobalt were taken as examples for the intra-laboratory comparison. Pearson's Product Moment Correlation yielded highly significant correlations with $R \geq 0.757$ ($P < 0.0001$) for all the comparisons. The good correlation between the two DET profiles of Fe, Mn and Co in sediment cores at Warneton is also visible in Fig. 2a–c. The moving average method was applied to the initial data resulting in a limited smoothing of the original profiles.

Table 2

Blanks and concentration ranges observed with DET and DGT probes (VUB and USTL)

Element	DET blank		DET observed range		DGT blank VUB		DGT blank USTL		DGT observed range	
	VUB ($\mu\text{g l}^{-1}$)	USTL ($\mu\text{g l}^{-1}$)	VUB ($\mu\text{g l}^{-1}$)	USTL ($\mu\text{g l}^{-1}$)	(ng cm^{-2})	($\mu\text{g l}^{-1}$)	(ng cm^{-2})	($\mu\text{g l}^{-1}$)	VUB ($\mu\text{g l}^{-1}$)	USTL ($\mu\text{g l}^{-1}$)
Cd	0.22±0.04	0.23±0.02	<dl–11	0.14–8.3	0.017±0.006	0.004±0.001	0.02±0.009	0.004±0.001	0.0–0.85	0.05–0.74
Pb	5.60±0.97	3.92±0.61	<dl–62	<dl–62	0.43±0.21	0.070±0.034	0.40±0.1	0.06±0.016	0.9–1	0.36–5.48
Mn	9.66±2.60	1.24±0.31	630–4900	144–3218	0.35±0.24	0.076±0.054	1.30±0.62	0.23±0.11	190–750	393–1560
Fe	197±51	476±73	170–42000	<dl–86000	4.9±3	1.019±0.771	17.17±8.6	2.91±1.47	170–1800	71–5270
Co	0.28±0.13	0.26±0.19	0.34–4.2	0.9–3.8	0.019±0.009	0.004±0.002	0.029±0.007	0.006±0.001	0.08–0.37	0.09–0.88
Ni	77±6	17±8	<dl–1800	<dl–58	3.16±1.13	0.69±0.25	2.96±1.4	0.63±0.3	0.43–17	1.14–10.99
Cu	6.6±2	14.7±0.21	<dl–100	6–73	0.73±0.29	0.15±0.06	2.73±0.46	0.54±0.09	0.400–5.5	1.54–6.25
Zn	173±61	39±4.4	<dl–1000	<dl–360	16±4	3.3±0.9	12±4	2.5±0.8	2–650	6.48–88.4
As	0.14±0.05		0.6–13							
Cr		4.9±2.1		<dl–20						

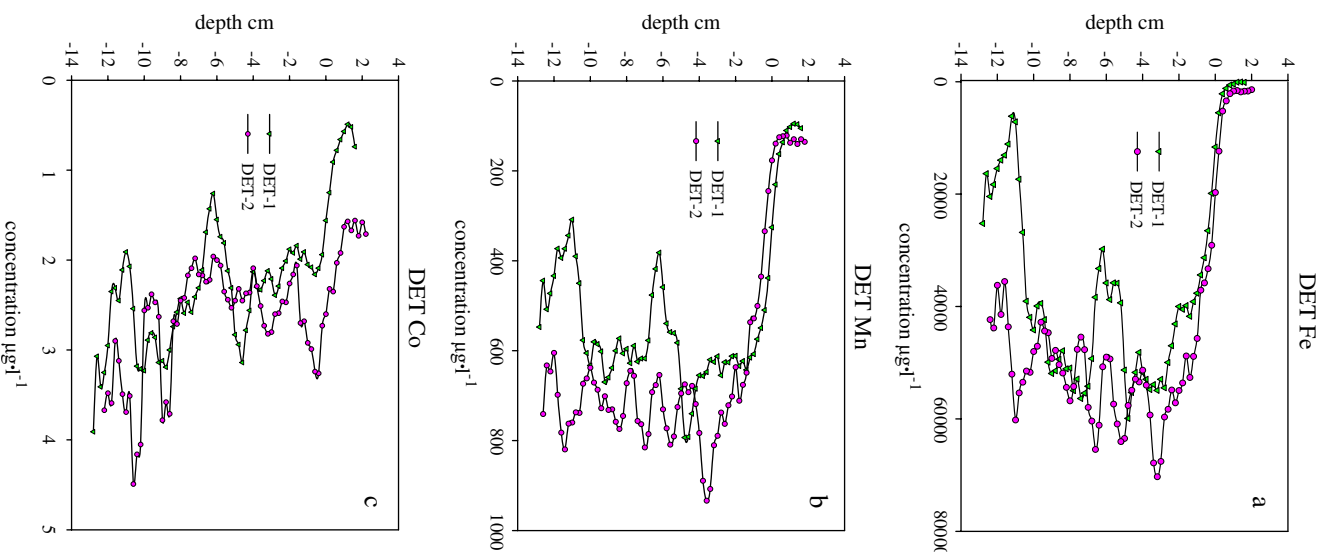


Fig. 2. Depth profiles of Fe (a), Mn (b) and Co (c) obtained from two DET probes at sampling station Warneeton.

Similarly to the DET profiles, DGT profiles were also determined in the sediment cores at Warneeton, and as an example the profiles of Fe, Mn, Co and Cu are discussed for the intra-laboratory comparison (Fig. 3a–d). Pearson's Product Moment Correlation yielded significant correlation with $R \geq 0.718$ ($P < 0.0002$) for all the comparisons. In addition, the moving average

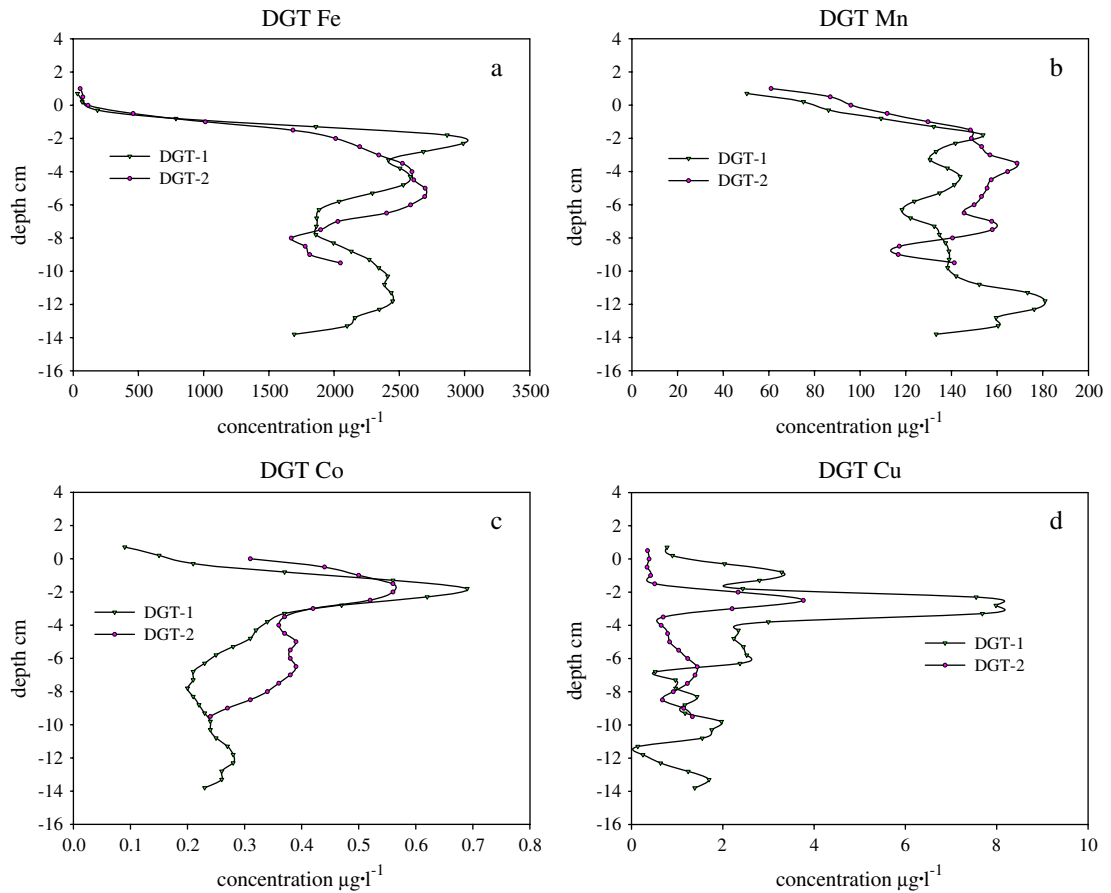


Fig. 3. Depth profiles of Fe (a), Mn (b), Co (c) and Cu (d) obtained from two DGT probes at sampling station Warneton.

method was performed on the initial trace metal data, smoothing the original profiles. The differences in DET and DGT profiles observed between two sediment cores can be explained by sediment heterogeneity as reported by Shuttleworth et al. (1999) and Fones et al. (2004).

3.3.2. Inter-laboratory comparison between VUB and USTL

Trace metal profiles in the sediments of the Helkijn sampling station were assessed both by Vrije Universiteit Brussels (VUB) and Université des Science et Technologie de Lille (USTL), thus performing an inter-laboratory comparison of the gel techniques. For most metals a good agreement was obtained between the two laboratories (see for example also Leermakers et al., 2005). One of the more difficult elements is iron because of the high sensitivity of Fe^{2+} to oxidants; therefore, we show here these profiles in some more detail. The smoothed profiles of Fe obtained by VUB and USTL with the DET and also the DGT samplers show the same features. In view of spatial heterogeneity in sediment

composition, the agreement between the two laboratories is fairly good (Fig. 4a–b).

The depth profiles of Fe obtained from the DET and DGT samplers by the two laboratories (Fig. 4a–b) show comparable trends, whereas the concentrations are not exactly the same. The reduction zones of Fe for both DET and DGT samplers, starts from the interface until around 7–8 cm depth; this was observed in the two laboratories. Oxygen depletion in Helkijn riverine pore waters explains those results. The reducing conditions benefit the dissolution of Fe(III) to Fe(II), the reduced Fe(II) species being much more soluble than the solid Fe(III)-oxides. The concentrations of Fe obtained by the DET technique are much higher (10 times for USTL and 40 times for VUB) than those obtained by DGT but also by centrifugation (results not shown). No direct explanation for the lower factor (10) observed by USTL is available except for sediment heterogeneity. In the pore waters of the river Rupel, which is a tributary of the river Scheldt (Leermakers et al., 2005), Fe concentrations observed with DGT were also a factor

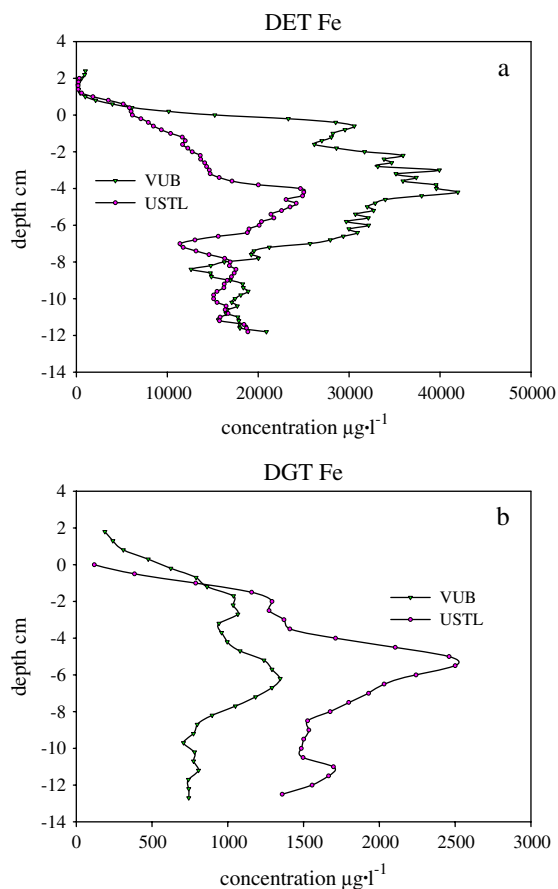


Fig. 4. Depth profiles of Fe obtained by DET (a) and DGT (b) from two laboratories at sampling station Helkijn.

10 lower than observed with DET. As explained in many articles (Davison and Zhang, 1994; Harper et al., 1998; Fones et al., 2004), DET and DGT concentrations are different due to (1) the sampling of different kinds of species (labile versus non-labile) and (2) the resupply rate for DGT.

4. Discussion

4.1. Warneton sampling station

4.1.1. Redox potential profiles

The redox potential profile (Fig. 5) shows a completely anoxic environment for the Warneton sediment. The redox values in the whole core (25 cm depth) were around -300 to -400 mV compared to the Ag/AgCl redox couple. This is confirmed by the absence of oxygen (unpublished results) and the very low nitrate concentration (around detection limit) from the sediment interface to the bottom of the sediment

core. The depletion of oxygen in the pore waters at Warneton is also responsible for the increase or production of iron(II) and manganese(II), two redox-sensitive elements involved as electron acceptors in the degradation of organic matter, from just below the interface. The maximum concentrations of Fe and Mn, for both DET and DGT samplers, appear at a depth of around 4 cm beneath the interface in the two sediments, but remain high in fact (much higher than the concentrations in the overlying water column) until the bottom of the core.

The DGT depth profiles for Fe, Mn, Co and Cu in the two sediment cores compare very well regarding their shape: production (increase) and consumption (decrease) zones are found at the same sediment depth layers. However, the intensity of the production–consumption process can differ significantly. For example, the Cu concentration maxima at about 2.5 cm depth (Fig. 3d) differ by a ratio of 1 to 2. The concentrations of Fe, Mn and Co obtained with the DET technique (Fig. 2a–c) are significantly higher than those resulting from the DGT technique (Fig. 3a–c).

4.1.2. Pore water measurements

Compared to the classic centrifugation technique, the concentrations of trace metals in pore water obtained by DET are much higher, especially for Fe. The most plausible reason to explain these differences is that despite the use of oxygen-free glove-bag for handling the cores during sectioning and centrifugation, oxygen still comes into contact with the pore water and oxidizes dissolved Fe(II) into solid Fe(III). Other trace elements, except Fe, Mn and Co were not available with the DET technique, because of the high blank values of the agarose gel compared to the naturally occurring

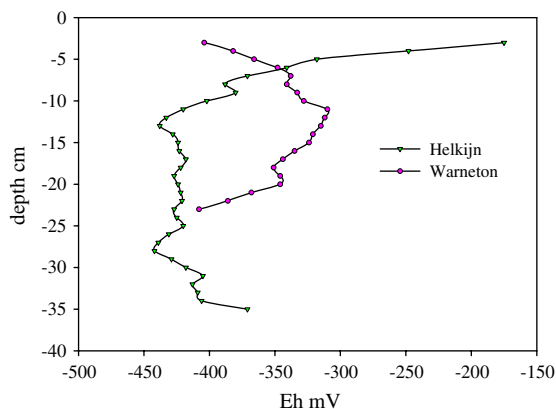


Fig. 5. Redox potential profiles in sediment pore waters at sampling stations Warneton and Helkijn.

concentrations (see also Table 2). Compared to the centrifugation or classic technique, the concentrations of Fe obtained by the DGT technique are slightly higher, but the latter concentrations are about a factor of 10 lower than the concentrations resulting from the DET technique. The concentrations of Cd, Pb Mn, Co, Ni, Cu and Zn obtained by the DGT technique are between 2 and 4 times lower than those resulting from centrifugation. Comparison between the centrifugation or classical technique and the DGT technique should be carried out with caution. DGT measures the localized interfacial concentration (this is depleted due to metal uptake by the DGT probe) in a very small volume of sediment adjacent to the DGT probe, whereas classical techniques measure bulk pore water concentration averaged from a much bigger volume (100 to 1000 times bigger) of sediment. While the profiles of Fe and Mn obtained with the DET probes are more or less similar (see Fig. 2a–b), that of Co differs in the deeper layers (below 6 cm depth) where it steadily increases (Fig. 2c). In contrast, the DGT profiles of Co decrease below 4 cm while those of Fe and Mn remain more or less constant in the same depth layers (Fig. 3a–c). The DGT profiles of Cu show a pronounced maximum at 2–4 cm of depth (Fig. 3d).

When pore water concentrations are measured independently by an alternative technique, DGT observed results can be expressed in terms of a ratio R (DGT/DET or DGT/centrifugation, with $0 < R < 1$) (Harper et al., 1998). In our case, the ratio R can be described as the average metal concentration from DGT divided by the average metal concentration from DET or centrifugation (Table 3). The R values (based on DGT/centrifugation unless otherwise indicated) for trace elements show us the following order: Fe (>1) > Mn (0.59) > Cu (0.52) > Pb (0.49) > Cd (0.44) > Zn (0.40) > Mn (0.23 DGT/DET) > Cr (0.23) > Co (0.20) > Ni (0.19) > Co (0.13 DGT/DET) > Fe (0.05 DGT/DET). The differences between centrifugation or DET and

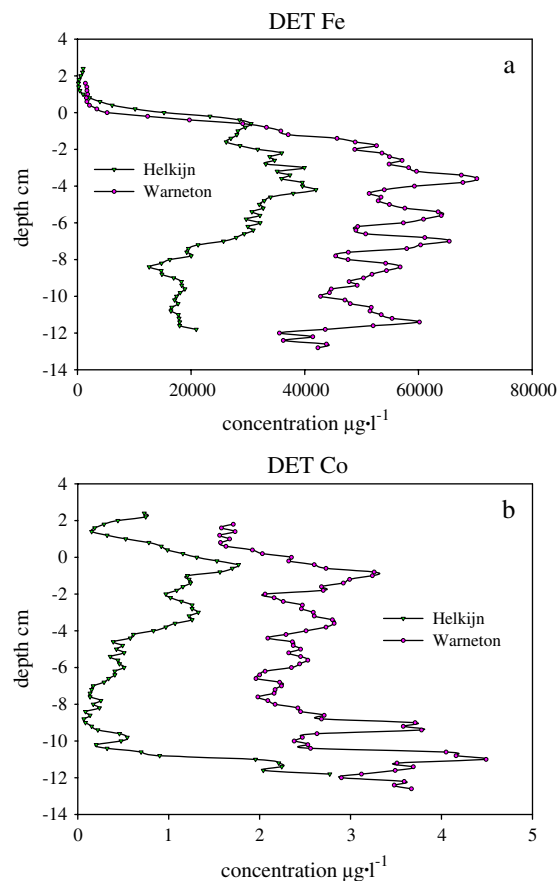


Fig. 6. Depth profiles of Fe (a) and Co (b) obtained from DET at Helkijn and Warneton.

DGT can be due to several factors such as for example the pore size of the gels (about 20 nm for DET and 2 nm for DGT), the competition between the DGT resin and complexing ligands when metal complexes are abundant, depletion of the pore waters during DGT sampling and so on. There is a large difference in R values when using Fe concentrations from DET probes or from centrifugation. As explained before, slight contact with oxygen during centrifugation will strongly reduce the dissolved Fe levels. The close R values of Ni and Co can point towards a similar chemistry and mineralogy of Ni and Co and also indicate similar release of labile Co and Ni.

4.2. Helkijn sampling station

4.2.1. Redox potential profiles and pore water measurement

The redox potential profile at Helkijn (Fig. 5) differs from that observed at Warneton, especially in the top 10 cm of the sediment. It decreases from about -170 mV at

Table 3

R value obtained at the Warneton sampling station

Trace metal	Average concentration ($\mu\text{g l}^{-1}$) DET	Average concentration ($\mu\text{g l}^{-1}$) centrifugation	Average concentration ($\mu\text{g l}^{-1}$) DGT	R value DGT/centrifugation (DET)
Cd	–	0.16	0.069	0.44
Pb	–	1.3	0.65	0.49
Mn	566	222	132	0.59 (0.23)
Fe	39001	1151	1825	>1
Co	2.4	1.6	0.33	0.20 (0.13)
Ni	–	8.7	1.7	0.19
Cu	–	3.0	1.6	0.52
Zn	–	46	19	0.40

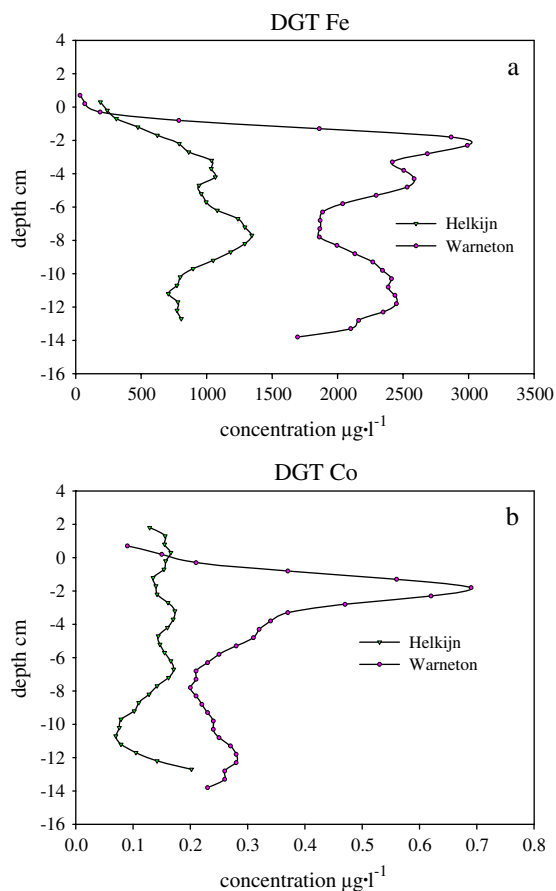


Fig. 7. Depth profiles of Fe (a) and Co (b) obtained from DGT at Helkijn and Warneton.

3 to 4 cm depth to about -400 mV at 10 cm depth. Further downwards, the redox remains relatively stable, with minor fluctuations, around a value of -420 mV. For interpretations of major and minor element profiles at Helkijn, it is thus important to notice that the upper sediment is gradually changing from a sub-oxic to a complete anoxic system. The concentration of nitrate for example decreased very fast from about 35 mg l^{-1} to the detection limit. The sub-oxic conditions in the first 10 cm of the sediments at Helkijn result in trace metal profiles showing different trends from those obtained at Warneton. The DET profile of Fe at Warneton is significantly higher than the one at Helkijn and the depth range of increased concentration is also much broader: from 2 to 14 cm at Warneton and from 2 to 7 cm at Helkijn (Fig. 6a). Similar results for Co were observed, except that from 8 to 10 cm depth on, the Co concentrations again increase (this was not the case for Fe), both at Warneton and at Helkijn (Fig. 6b).

The similar behavior of, or at least the strong correlation between, the total dissolved Co and Fe

concentrations (including colloidal species) at Helkijn and Warneton for the upper 8–10 cm, confirms their similar redox sensitive characteristics (Fig. 6a–b). In the deeper layers, this is no longer true. There, total dissolved Fe does not show any particular features, while total dissolved Co increases, especially at Helkijn. This is also observed by the DGT technique (Fig. 7a–b).

The DGT profile of Fe and the corresponding concentration gradient at Helkijn is also much lower than the one at Warneton (Fig. 7a). This is probably linked to the much larger redox gradient in the upper sediment at Warneton. In addition, the DGT profile of Co agrees much better with the Fe DGT profile at Warneton than at Helkijn (Fig. 7a–b). Both DET and DGT Co profiles are very similar in the deeper layers at Helkijn.

Compared to the concentrations obtained by the centrifugation technique, the concentrations of Fe resulting from the DET technique are more than 10 times higher (Davison et al., 2000). This is less in the case for Mn and Co, and was also observed at Warneton.

The R values were also calculated at Helkijn (Table 4) similar to what was done at Warneton. The R values indicated the following order: Fe (0.46) > Zn (0.40) > Pb (0.31) > Co (0.26) > Mn (0.22) > Co (0.17 DGT/DET) > Mn (0.15 DGT/DET) > Cu (0.10) > Ni (0.08) > Fe (0.04 DGT/DET) > Cd (0.03). Compared to Warneton, the R values of Fe, Cd and Cu strongly decreased while only that of Co (for both expressions of R) increased slightly.

4.2.2. Metal concentration gradients at the water–sediment interface

The high resolution profiles obtained with the DET and DGT probes provide much more accurate estimates of the metal concentration gradients at the water–sediment interface than those obtained by the classic centrifugation technique. It is clear that these concentration gradients are spatially specific and that 2-D DET

Table 4
 R value obtained at the Helkijn sampling station

Trace metal	Average concentration ($\mu\text{g l}^{-1}$) DET	Average concentration ($\mu\text{g l}^{-1}$) centrifugation	Average concentration ($\mu\text{g l}^{-1}$) DGT	R value DGT/centrifugation (DET)
Cd	–	5.1	0.14	0.03
Pb	–	8.0	2.3	0.31
Mn	2251	1532	331	0.22 (0.15)
Fe	20952	1795	833	0.46 (0.04)
Co	0.83	0.54	0.14	0.26 (0.17)
Ni	–	17	1.2	0.08
Cu	–	11	0.98	0.10
Zn	–	64	28	0.40

and DGT probes (eventually even cylindrical) should be used to calculate more reliable fluxes for that area (see also Fones, 1998). Our intention is only to illustrate the error that may result from the use of low-resolution profiles. Iron and manganese gradients at the water–sediment interface calculated from the DET profiles and those calculated from classic centrifugation profiles at Warneton were compared. For both metals, the subsurface concentration gradients obtained from the DET probes are much higher than those obtained by the classic centrifugation. Large over- or underestimation of epibenthic fluxes can result from the use of low resolution profiles and this is not only valid for metals but also for nutrients, organochlorine compounds, etc.

5. Conclusion

In sediment pore waters of Helkijn and Warneton sampling stations (rivers Scheldt and Leie, Belgium), major cations and anions were determined after conventional sectioning of the core and centrifugation of the slices. The balance was very good at Warneton (differences are less than 10%), somewhat less good at Helkijn with a largest difference of 20%.

High DET or DGT blanks can sometimes hamper the assessment of trace metal profiles in relatively low polluted aquatic sediments. Comparing the DET blanks with metal concentration ranges observed in the sediment cores at Helkijn and Warneton stations, it appears that the concentrations of some elements in sediment cores are sometimes lower than the blanks. The concentration ranges observed with the DGT gels at Helkijn and Warneton stations, were only for the lowest Ni and Zn concentrations at the limit of quantification.

In order to validate the DET and DGT techniques, intra- and inter-laboratory comparisons were carried out. For the intra-laboratory comparison, two couples of DET and DGT probes arranged back to back were inserted into two sediment cores close to each other. The DET as well as DGT profiles were very similar in magnitude and shape. The inter-laboratory comparisons were carried out at Helkijn. The smoothed profiles of Fe obtained by VUB and USTL with the DET and also the DGT samplers show the same features. In view of spatial heterogeneity in sediment composition, the agreement between the two laboratories is fairly good.

The results observed at Warneton and Helkijn were also compared. The redox potential profile at Helkijn differs from that observed at Warneton, especially in the top 10 cm of the sediment. At Warneton, the redox potential profiles show a completely anoxic sediment environment. At Helkijn, the redox dec-

reases from about -170 mV at 3 to 4 cm depth to about -400 mV at 10 cm depth. Further downwards, the redox remains relatively stable, with minor fluctuations, around a value of -420 mV. For interpretations of major and minor element profiles at Helkijn, it is thus important to notice that the upper sediment is gradually changing from a sub-oxic to a complete anoxic system, while at Warneton it is immediately completely anoxic.

The DET profile of Fe at Warneton is significantly higher than the one at Helkijn and the depth range of increased concentration is also much broader: from 2 to 14 cm at Warneton and from 2 to 7 cm at Helkijn. Similar results for Co are observed, except that from 8 to 10 cm depth on, the Co concentrations again increase (this was not the case for Fe), both at Warneton and at Helkijn. The DGT profile of Fe at Helkijn is also much lower than the one at Warneton, while the concentration gradient at Helkijn is much smaller than at Warneton. This is probably linked to the much larger redox gradient in the upper sediment at Warneton. In addition, the DGT profile of Co agrees much better with the Fe DGT profile at Warneton than at Helkijn. Both DET and DGT Co profiles are very similar in the deeper layers at Helkijn. Compared to the concentrations obtained by the centrifugation technique, the concentrations of Fe resulting from the DET technique are more than 10 times higher. This is less the case for Mn and Co, and is similar to the results from Warneton.

We have also shown that large over- or underestimation of epibenthic fluxes can result from the use of low resolution profiles.

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