Geochemical behavior of trace elements in sub-tidal marine sediments of the Belgian coast

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ABSTRACT

High resolution profiles of trace elements (Fe, Mn, Co, As, Cu, Cr, Ni and Pb) were assessed using the DET (Diffusive Equilibrium in Thin films) and DGT (Diffusive Gradients in Thin films) techniques in silty, organically enriched, sub-tidal sediments of the Belgian coast during late winter and spring 2008. The general chemical properties of the sediments such as dissolved oxygen, pH, Eh and sulfide profiles, controlling precipitation/mobilization reactions, were determined with electrodes (pH and Eh) and microelectrodes (oxygen) and AgI-DGT probes (sulfide).

Most trace elements show subsurface maxima and low concentrations beneath 8 cm of depth. The main physicochemical parameters controlling the vertical concentration profiles are dissolved oxygen and redox potential in the surface sediment and sulfide in the deeper sediment layers. Thermodynamic equilibrium calculations have been carried out verifying which solid phases can explain the dissolved trace metal concentrations. Seasonal variations of trace elements have been observed during the sampling period and sedimentation of fresh particulate organic matter (POM) derived from phytoplankton blooms appear to be the main cause of this temporal variability.

Flux calculations based on DGT profiles (these fluxes are minimum ones) show that exchange fluxes of trace metals in February are slightly higher than in April. In addition, "DGT pistons" were deployed at the sediment water interface (SWI) to accumulate labile ions from below. This way all labile ions, binding onto the DGT Chelex resin, are pumped out of the pore waters and the solid sediment phase (only the mobile fraction). These results are a direct estimation of the amount of trace elements that can be released from the upper sediment to the water column (in the range of $4.4 \cdot 10^{-5}$ to 0.10 mmol·m^{-2}·d^{-1} for Co, Pb, Cr, As, Cu, Ni, Fe and Mn).

1. Introduction

Many coastal areas worldwide are contaminated by trace metals such as Cd, Cu, Pb, Zn, Hg and Ni and these contaminants may accumulate in sediments. On the Belgian Continental Plate (BCP) trace metal concentrations in sediments are at or above the Ecotoxicological Assessment Criteria (EAC) as defined by the OSPAR Commission as concentration levels below which no harm to the environment or biota is expected (QSR 2000). In addition, many metals on the European Union's list of priority substances for the Water Framework Directive (2000/60/EC) which accumulate in sediments may be solubilized allowing for diffusion back to the water column. Numerous biogeochemical transformations as well as redox, pH, sulfide, oxygen influence the distribution of trace metals between solid to liquid phase at and below the sediment water interface (SWI) (Masscheleyn et al., 1991, 1992; Patrick and Jugsujinda, 1992; Van Ryssen et al., 1998). The Belgian coastal zone of the North Sea is an area that is strongly influenced by eutrophic rivers such as Scheldt, Rhine and Meuse resulting in phytoplankton blooms, mainly composed of diatoms and prymnesiophyte *Phaeocystis* (Muylaert et al., 2006). Spring blooms begin in March when nutrient, light and temperature conditions become sufficient for phytoplankton growth and terminate in April–May with the onset of nutrient limitation, after which large amounts of organic material sediment out (Baeyens et al., 1984; Rousseau et al., 2000; Muylaert et al., 2006). As a consequence, the degradation of increasing amounts of freshly deposited organic matter changes the physicochemical conditions in the sediments potentially releasing trace metals from the solid into the dissolved phase (Gao et al., 2006; Pakhomova et al., 2007).

Characterization of rapidly changing physicochemical conditions in complex aquatic sediments, such as oxygen and redox, demands minimal disturbance to the system when sampling. Suitable sampling

tools, respecting the initial in situ conditions in aquatic sediments, are the following: Diffusive Equilibrium in Thin Films (DET) and Diffusive Gradients in Thin Films (DGT). Presently found in Davison et al., 2000, while more specific information about high resolution profiles in sediment pore waters is reported by Zhang et al. (1995), Fones et al. (2001, 2004) and Zhang et al. (2002). Briefly, DET compares with the technique of dialysis peepers (vertical set of dialysis cells), but instead of putting a solution in the compartments, it uses a gel that equilibrates much faster (Davison et al., 1991). With this technique no preconcentration is obtained, nor a selection of compounds, as long as the pore size allows diffusion (solutes should generally be smaller than 20 nm), thus total dissolved phase is available. The DGT technique, based on mass transport control of metals has been inserted vertically in sediment pore waters by several researchers (Zhang et al., 2002; Fones et al., 2004; Leermakers et al., 2005; Gao et al., 2006, 2007) to determine high resolution profiles. It makes use of two hydrogel layers: a polyacrylamide gel covered with a membrane (0.45 µm) is used as the diffusive layer, and is backed up by a second thin gel layer containing a Chelex cation-exchange resin selective for metals. With this technique, only the labile metal fraction small enough to diffuse through the gel and capable of binding to the resin layer is assessed.

Once high resolution profiles of trace metals are assessed in the sediment pore waters with these probes, one can also estimate the gradients and hence the exchange fluxes at the sediment water interface (SWI). The trace metal outflux from the sediment can also be estimated using a "DGT piston". This "DGT piston" is a DGT probe, based on the same principle as explained above, but placed face down at the SWI with above several cm of overlying water. Hence, this set-up maximizes in a certain way the pore water gradient at the interface because the concentration at the SWI is zero.

The novelty of this study is two-fold: (1) The different approaches we use to assess exchange fluxes at the sediment water interface in the marine environment (flux calculations based on high resolution profiles and direct flux estimations with a DGT piston) are seldom applied and (2) until now, no reliable Ks/IAP values for Fe sulfides exist at non-acidic pH (Rickard and Morse, 2005). Also for other trace metals they are rare. Therefore, good field data of dissolved trace metals and sulfide are required. This study contributes to a currently empty of data set.

2. Materials and methods

High resolution pore water profiles of trace metals were assessed with DET and DGT probes, of sulfide with a DGT-AgI probe, and of relevant physicochemical parameters (Eh, pH, O_2) with electrodes. Particulate organic carbon (POC) and carbon/nitrogen isotope ratios were analyzed with an IRMS (Delta$^+$XL Isotope Ratio Mass Spectrometer Thermo Finnigan) and a C/N analyzer.

2.1. Sediment sampling collection

Integral sediment samples were collected at Belgian coastal station 130 (Fig. 1) with a Reineck core ($\varnothing = 15$ cm). Plexiglas tubes ($\varnothing = 7$ cm) were carefully inserted in the sediment of the Reineck and slowly retrieved allowing 5–10 cm overlying water to remain above the sediment, from these sub-cores multiple data were collected: 1) the assessment of trace metal profiles by applying DET and DGT probes and sulfide profiles by using a DGT-AgI probe; 2) direct flux measurements by using "DGT pistons" and 3) the assessment of oxygen, pH and Eh profiles with electrodes.

2.2. Measurement of oxygen, pH and redox potential

Dissolved oxygen measurements were performed by amperometry using a Clark microelectrode ($\varnothing = 500$ µm, UNISENSE) connected to a high-sensitivity picoammeter (PA 2000 picoammeter, UNISENSE). The oxygen microsensor is linked to a micromanipulator in order to carry out millimetric profiles at the sediment water interface (SWI). To set
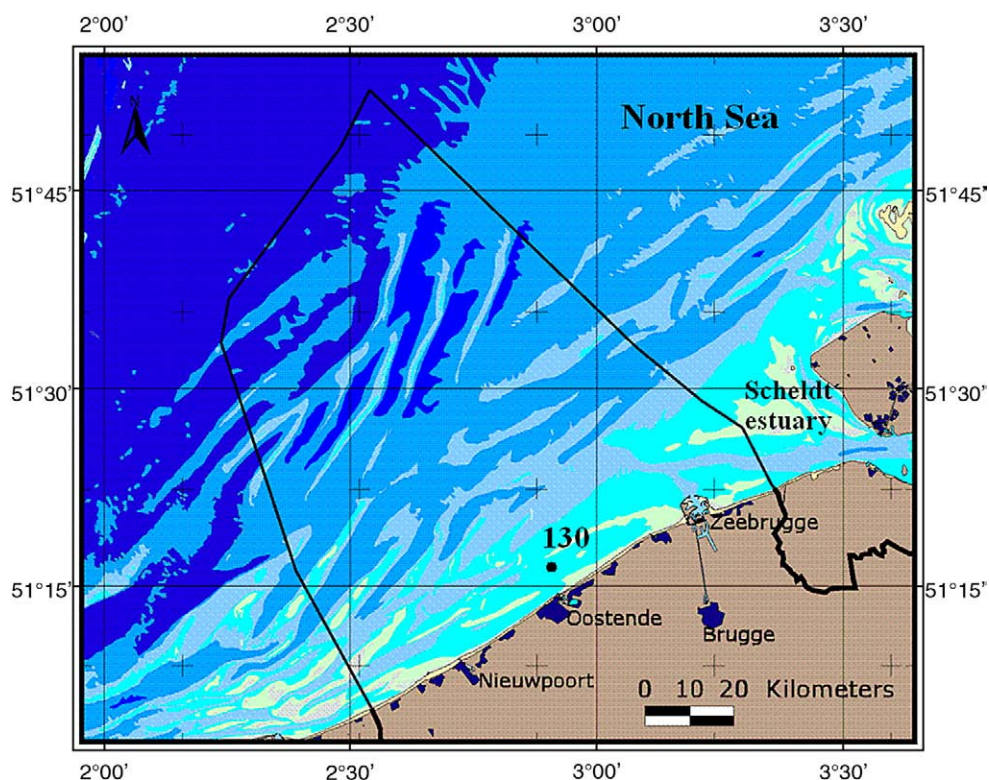

Fig. 1. Sampling map.

the full scale range an O_2 free solution was used to set zero and a well aerated solution bubbled with air where temperature and salinity conditions of the calibration solutions correspond to those in the field.

Eh and pH measurements were performed using a combined redox electrode with an Ag/AgCl, ([KCl] = 3 M) reference electrode and a pH combined electrode. All potential values further in this paper, refer to the Ag/AgCl electrode. The pH electrode is calibrated with Merck buffers, type NBS (National Bureau of Standards). In addition, since measurements are carried out in seawater, a correction of the values was made according to Aminot and Kerouel (2004).

2.3. Analysis of POC, $\delta^{13}C$ and $\delta^{15}N$ in top layer sediments

Dried fine sediment powder was used for POC, $\delta^{13}C$ and $\delta^{15}N$ analysis. Subsamples for elemental (POC) and bulk stable isotope composition were acidified with dilute (5%) HCl before analysis to remove carbonates. $\delta^{13}C$, $\delta^{15}N$ and POC were determined by combusting preweighed samples in a Carlo-Erba elemental analyzer coupled to a conflo-interface to an IRMS (Finnigan Delta-Plus XL) (Bouillon et al., 2004). Acetanilide, IAEA-CH6 and IAEA N1 were used for the calibration of POC, $\delta^{13}C$ and $\delta^{15}N$ analysis. RSD values are 4% for POC, 0.4‰ for $\delta^{15}N$ and 0.2‰ for $\delta^{13}C$.

2.4. Preparation of DET and DGT devices

The DET probe preparation was similar to that proposed by Docekalova et al. (2002). Briefly a gel containing 1.5% agarose was prepared and placed in a boiling water bath. After dissolution, the solution was immediately pipetted into a preheated constrained DET probe and allowed to cool and set, the constrained DET probe's material was obtained from DGT Research Ltd. The gels were then covered with a 0.45 µm cellulose acetate filter (Millipore), finally, the window plate was put on top of the probe and all elements gently pressed together.

The preparation of "DGT pistons" and probes was carried out according to the protocol from Lancaster (www.dgtresearch.com). The "DGT pistons" (DGT Research Ltd) were 2.5 cm diameter with a window of 2.0 cm diameter and the DGT probes (DGT Research Ltd) were 180 mm · 40 mm, with a window of 150 · 18 mm open to the sediment. Agarose–polyacrylamide hydrogel consisting of 15% acrylamide (Merck) and 0.3% agarose derived cross linker (DGT Research Ltd) was used as a diffusive gel. Ion exchange resin (Chelex 100) with a bead size of 200–400 Mesh (Biorad) was used as the binding agent.

Before deployment, DET/DGT probes and DGT pistons were de-oxygenated by immersing them for 24 h in a container with trace metal cleaned (5–10 g Chelex-100 were added for removing trace metals) artificial sea water (Fones et al., 2004).

2.5. Preparation of DGT-AgI probe

The DGT-AgI probe is similar to the DGT-Chelex probe, only AgI is used here as the binding agent. It was prepared according to the procedure of DeVries and Wang (2003). After the preparation of the DGT-AgI probe, it is immersed in a 0.01 M NaNO$_3$ solution and purged with N$_2$ during 24 h before deployment in the sediment (Teasdale et al., 1999). The accumulation of sulfides occurs according to the following equation (Teasdale et al., 1999): AgI (white) + HS$^-$ → Ag$_2$S (white to black) + H$^+$ + 2I$^-$. Calibration curves are carried out in an oxygen free glove box (under N$_2$) and in the dark, with "DGT pistons" (Lancaster Research Ltd) exposed to de-oxygenated standard sulfide solutions (pH = 9), ranging from 0 to 100 µM. The sulfide standard solution was prepared from Na$_2$S·9H$_2$O (Aldrich) also under nitrogen atmosphere and daily titrated (potentiometry) with a Cd^{2+} standard solution, by using a sulfide ion-selective electrode (Orion) and an Hg/Hg$_2$SO$_4$ reference electrode. Each AgI resin is then dried and analyzed following the same protocol as for the other DGT-AgI probe types.

Finally, the sulfide concentration is determined as a function of the gray scale density related to each standard.

2.6. Deployment and retrieval of DET and DGT probes

A couple of DGT probes, respectively of 0.80 mm and 1.2 mm diffusive gel thickness and, arranged back to back, was inserted into one large sediment core (7 cm) together with another couple of DET and DGT-AgI probe, also arranged back to back in the sediments for 6 h. The core was held inside a container which had a continuous flow of sea water. After deployment, the DET gels were extracted from the small slits of the probe, while the resin gel from DGT probes was cut into 5-mm intervals using a Plexiglas gel cutter. Each gel slice from DET and DGT probes was then eluted in a 1 M HNO$_3$ solution and diluted for analysis by HR-ICP-MS (Thermo Finnigan Element II).

The DGT device is deployed for a fixed period of time (t) where after the accumulated mass of solute in the binding layer (M) is measured. For a known thickness of the diffusion layer (Δg), the mean concentration in solution can be calculated using Fick's law (Eq. (1)):

$$C_b = M \cdot \Delta g / D \cdot A \cdot t \qquad (1)$$

D is the diffusive coefficient of solute in diffusive gel, C_b is the concentration of solutes in bulk solution (pore water), Δg is the thickness of diffusive gel and A is the surface area.

In practice, the concentration gradient within the diffusive gel is often not constant during the DGT deployment period. Concentration C_b changes with time (Zhang et al., 1995) so the DGT measured concentration is interpreted as a time-average value of C_b.

$$c_{DGT} = \frac{1}{t} \int_{t=0}^{t} C_b(t_i) dt \qquad (2)$$

When two DGT probes with different gel thicknesses (Δg_1 and Δg_2) are deployed for the same period of time, it is possible to obtain information about the resupply of metals from the solid phase. From Eq. (1) we obtain two concentrations C_{b1} and C_{b2}. If the resupply of metals from the solid phase is sufficient to maintain the maximum flux (fully sustained case), then $C_{b1} = C_{b2}$. In the partially sustained case, the concentration using the thinner gel (which requires a higher flux) will be underestimated. If there is no resupply from the solid phase (unsustained case), the concentration gradient is mainly within the sediment, minimizing the effect of the diffusive gel. In that case $F(\Delta g_1) = F(\Delta g_2)$ and $\Delta g_1/\Delta g_2 = C_{b1}/C_{b2}$ (Zhang et al., 2002). The metal gradient is calculated based on the DGT profiles at the SWI. Then the exchange flux at the SWI is calculated by multiplying this gradient with the diffusion coefficient in the sediments. At coastal site 130 we used the diffusion coefficient of 10^{-5} cm^2 s^{-1} estimated earlier by Baeyens et al. (1986).

2.7. Deployment and retrieval of "DGT pistons"

During the cruises in 2008, remobilization fluxes of trace metals at the sediment water interface (SWI) were also estimated by "DGT pistons". These "DGT pistons" are placed diffusive gel down at the SWI with 5 cm overlying water. Oxygen intrusion was prevented by extending the device to the walls of the Plexiglas tube, covering the whole surface of the core. This set-up allows all labile ions that can bind onto the DGT resin, are vertically pumped out of the pore waters and eventually from the solid sediment phase (the mobile fraction) while reprecipitation of iron and manganese oxyhydroxides is avoided. The deployment times for DGT pistons are 2, 4 and 6 h respectively. After the withdrawal of "DGT pistons" from the sediment core, the resin gels inside the "DGT pistons" were eluted in 1 M HNO$_3$ solution and analyzed by HR-ICP-MS.
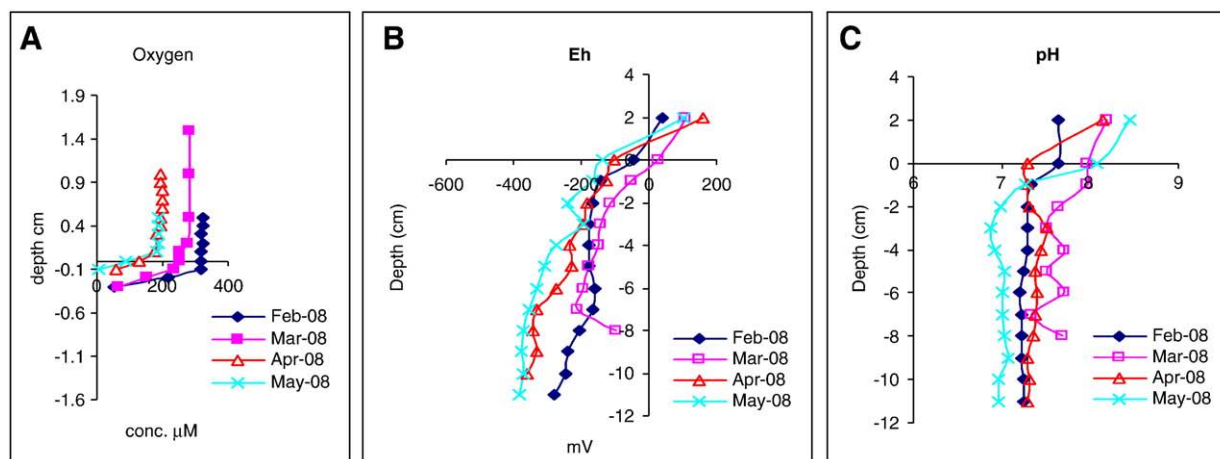
Fig. 2. Oxygen (A), redox potential (B) and pH (C) profiles from February to May 2008.

The metal flux (F) can be defined as the mass of metals (M), which diffuses through the diffusive gel with surface area (A) during the deployment time (t) and can be calculated from Eq. (3).

$$F = D \cdot dc / dx = D \cdot C_b / \Delta g = M / A \cdot t \qquad (3)$$

3. Results and discussion

3.1. Physicochemical parameters at station 130

Dissolved oxygen profiles indicate highest concentration during the winter months of February and March in overlying bottom waters and sediment pore waters (Fig. 2A). At 0.3 cm of depth the sediment becomes anoxic. This depth rises to 0.1 cm in the spring months of April and May (Fig. 2A). These results suggest an increased microbial activity in the sediment surface layer in the spring months, probably due to a supply of freshly produced organic matter. The POC results vary between 1.4 and 2.3% for the respective periods (Table 1). This variability can, however, be explained by a variable input from the Scheldt estuary outflow rich in organic matter, and by the spatial heterogeneity in sediment composition. Moreover, the lower percentage of POC during February to March cannot be due to bacterial degradation, because bacteria preferentially use the lighter isotopes, which would result in more positive $\delta^{13}C$ values of POC in the sediment instead of lower ones as observed for March. On the contrary, the isotope ratios of organic C suggest an input of freshly produced POC in March because $\delta^{13}C$ values decreased, in agreement with the lower $\delta^{13}C$ values of marine phytoplankton (Michener and Schell, 1994). The $\delta^{15}N$ values in sedimentary POC also decrease, but their interpretation is more difficult. The degradation of this organic matter in the following months is corroborated by a decrease in dissolved oxygen levels in the surface sediment layer (Fig. 2A) and by a progressive increase in $\delta^{13}C$ and $\delta^{15}N$ because the lighter isotopes are preferentially assimilated by the bacterial population (Blair et al., 1985). This progressive increase in the isotope ratios is in fact a balance between POC degradation and input of newly produced organic matter, with the

former process dominating the latter. The redox profiles corroborate the results obtained on dissolved oxygen, with lowest values in spring (−135 mV at the SWI and −372 mV at 10 cm of depth) (Fig. 2B). During the month of March pH values are the lowest and the most variable (Fig. 2C). In March dissolved sulfide levels remain always very low compared to other months, but in February concentrations rapidly increase from 5 μM at 8 cm up to 63 μM at 12.3 cm and remaining stable till the bottom of the sediment core (Fig. 3). Measurable amounts of S^{2-} were not present during April and May in the upper 6.5 cm of depth (Fig. 3). In April, they increase to 40 μM between 8 and 11 cm of depth, but drop then again below 5 μM, below 14 cm. In May, sulfide levels increase to a stable concentration of 40–80 μM between 8 and 12 cm of depth (Fig. 3). Seasonal variation in those physicochemical parameters induces temporal variation in some of the trace metal levels as we will see further in this paper.

3.2. High resolution profiles of trace elements assessed by DET and DGT probes and seasonal variation

Subsurface DET profiles (Figs. 4 and 5) show a range of concentrations from detection limits in deep layers to a maximum of 94 μM of

Table 1
$\delta^{15}N$, $\delta^{13}C$ and POC values in the sediment top layers.

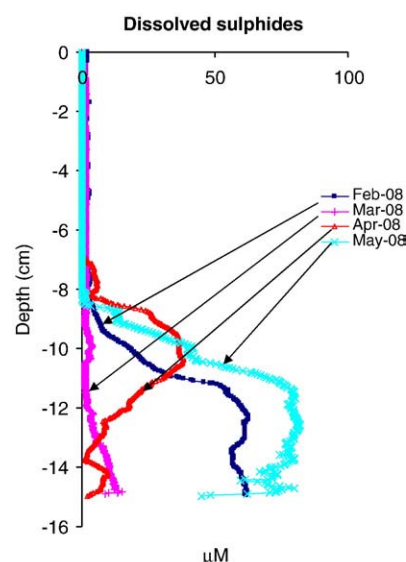| Month	$\delta^{15}N$ ‰	$\delta^{13}C$ ‰	POC %
Feb	9.93	−23.00	2.3
Mar	7.95	−23.41	1.4
Apr	8.46	−23.03	1.6
May	8.22	−22.62	1.7

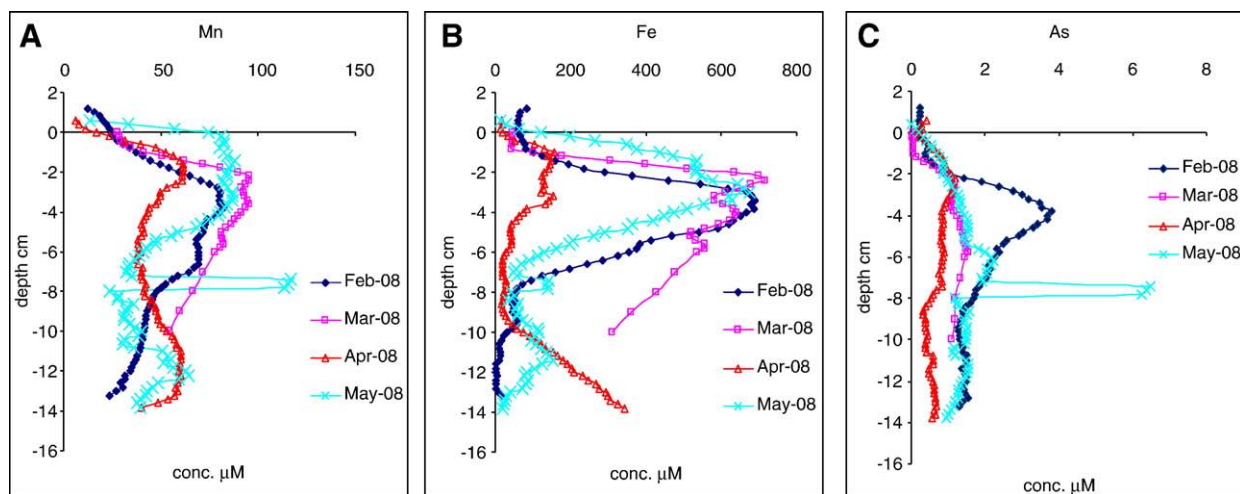**Fig. 3.** Dissolved sulfide concentration profiles from February to May 2008.

Fig. 4. Vertical profiles of Mn (A), Fe (B) and As (C) assessed by DET from February to May 2008.

Mn, 720 µM of Fe, 3.8 µM of As indicating a typical redox pattern for coastal marine sediments. Fe presents this pattern in relation to redox conditions (oxic, suboxic and anoxic). In the suboxic pore water layers (between 2 and 6 cm of depth), Fe oxides are reduced and total dissolved Fe levels (DET) reach a concentration of about 700 µM during all surveys, except that of April when the maximum only equals 160 µM (Fig. 4B).

In February and May when sulfide levels are important in the sediment layer below 8 cm of depth, low total dissolved Fe levels (DET) are observed, while in the other months Fe levels can reach 340 µM. The seasonal variability of the Mn profiles (DET) is much less pronounced than for Fe (Fig. 4A and B). In addition, in the deeper sediment layers, even with dissolved sulfide levels above 5 µM, dissolved Mn levels are still relatively high. In fact, this result is not really surprising, since the affinity of Mn for sulfides is relatively poor. Several publications have indeed shown MnS is not a solute observed in most pore waters (Canavan et al., 2007; Huerta-Diaz et al., 1998; Morse and Luther, 1999; Billon et al., 2001). Arsenic only shows an important suboxic maximum in February (DET) (Fig. 4C). Concentration profiles of Pb, Cr, Ni and Cu could not be assessed with the DET technique due to high concentrations in the agarose gel blanks.

The DGT technique gives a direct measurement of time averaged fluxes rather than concentrations. Concentrations can however, be estimated when (1) a constant pore water flux is maintained and (2) all compounds binding onto the resin have the same diffusion coefficient in the gel layer. The first condition means that there exists a sufficiently fast dissolution from the solid phase into the pore water. This can be checked by using DGT devices with different diffusive gel layer thickness. In 2008, at station 130, a test to determine trace element dissolution in sediments was performed using DGT probes with gel thickness of 0.8 mm and 1.2 mm. No systematic differences were observed between the concentrations found in the DGT probes (data not shown). The random differences between the two profiles, corresponding to the thinner and thicker gel layers, are within the error due to sample heterogeneity. We may thus assume that a constant pore water flux from solid to pore waters is maintained during the period of exposure. The second condition is much more difficult to prove in situ. In fact, free ions diffuse faster than complexes (Zhang, 2004) but what is the percentage of free ions, inorganic and organic complexes and what is the difference in diffusion rate between these species? Since the overall diffusion coefficient used in our pore water concentration calculation (Eq. (1)) is overestimated, the pore water concentration and hence the exchange fluxes are underestimated causing our reported fluxes to be minimum.

The labile Fe, Mn and As levels (DGT) show a similar profile to that observed with the DET except for the March profile of Fe, which after an initial, suboxic increase remains almost constant over the whole depth of the core (Fig. 5B). For Co, Pb, Cr, Ni and Cu, the profiles obtained from the DGT technique are shown in Fig. 5. Only Co and Ni show some suboxic maxima, while the Pb and Cr profiles present several high sporadic levels at various depths in March (for Cu this occurs in almost all months) caused either by local niches (heterogeneity) or analytical artifacts (Fig. 5E, F and H). In the <63 µm fraction of the solid phase in the surface sediment following concentrations are observed (all concentrations in µg g^{-1} dw): 20,000–23,000 (Fe), 620–780 (Mn), 55–65 (Cr), 26–33 (Ni), 13–16 (Cu), 25–32 (Pb), 7–10 (As), 0.36–0.48 (Cd) and 28,000–31,000 (Al) (http://www.mumm.ac.be/datacentre/).

This means that all elements are enriched versus Fe, ranging from 1.5 to 2.5 for Cr, Cu, Mn, Ni and Pb and up to 6 for As and Mn, As, Co and Ni also show a subsurface maximum. Trace elements are known to be associated with Fe oxides (via adsorption or co-precipitation) and can thus be co-released in the pore water together with Fe, due to the suboxic conditions created by diagenetic processes.

It is worthwhile to investigate seasonal effects of phytoplankton blooms (in surface sediment) and sulfide in the deeper sediment layer, on the trace metal profiles in the pore waters. The phytoplankton biomass at station 130 mainly composed of diatoms (De Bock & Sabbe, unpubl. data) was <1.5 µg chl-a L^{-1} until March, then gradually increased to approximately 16 µg chl-a L^{-1} by mid April. Based on the chl-a in the water column and the δ^{13}C–POC levels in sediments, we can assume that pore waters became enriched in newly supplied DOC (dissolved organic carbon)/POC (particulate organic carbon) in March–April potentially forming large Fe–organic complexes which are incapable of diffusing into the small pores of the DET and DGT gels (Davison and Zhang, 1994; Zhang and Davison, 1999), explaining the lower subsurface concentrations of Fe in April. The behavior of Mn and As is similar to Fe but less pronounced. For labile dissolved Fe (DGT), this is also valid in March (Fig. 5B). Another possible reason for low Fe could be the introduction of oxygen during DET and DGT deployment in April (the oxygen concentration at the SWI is then very low), but this should normally result in small colloidal Fe and Mn oxyhydroxides. Such small colloids are measured with the DET probe, but not with the DGT unless these colloids are very unstable. However, for Fe both the subsurface DET and DGT profiles are strongly reduced in April, suggesting that oxygen is not the key parameter causing the subsurface suppression in April.

In the deeper sediment layers dissolved sulfide clearly controls the dissolved trace metal contributions. In March higher concentrations of
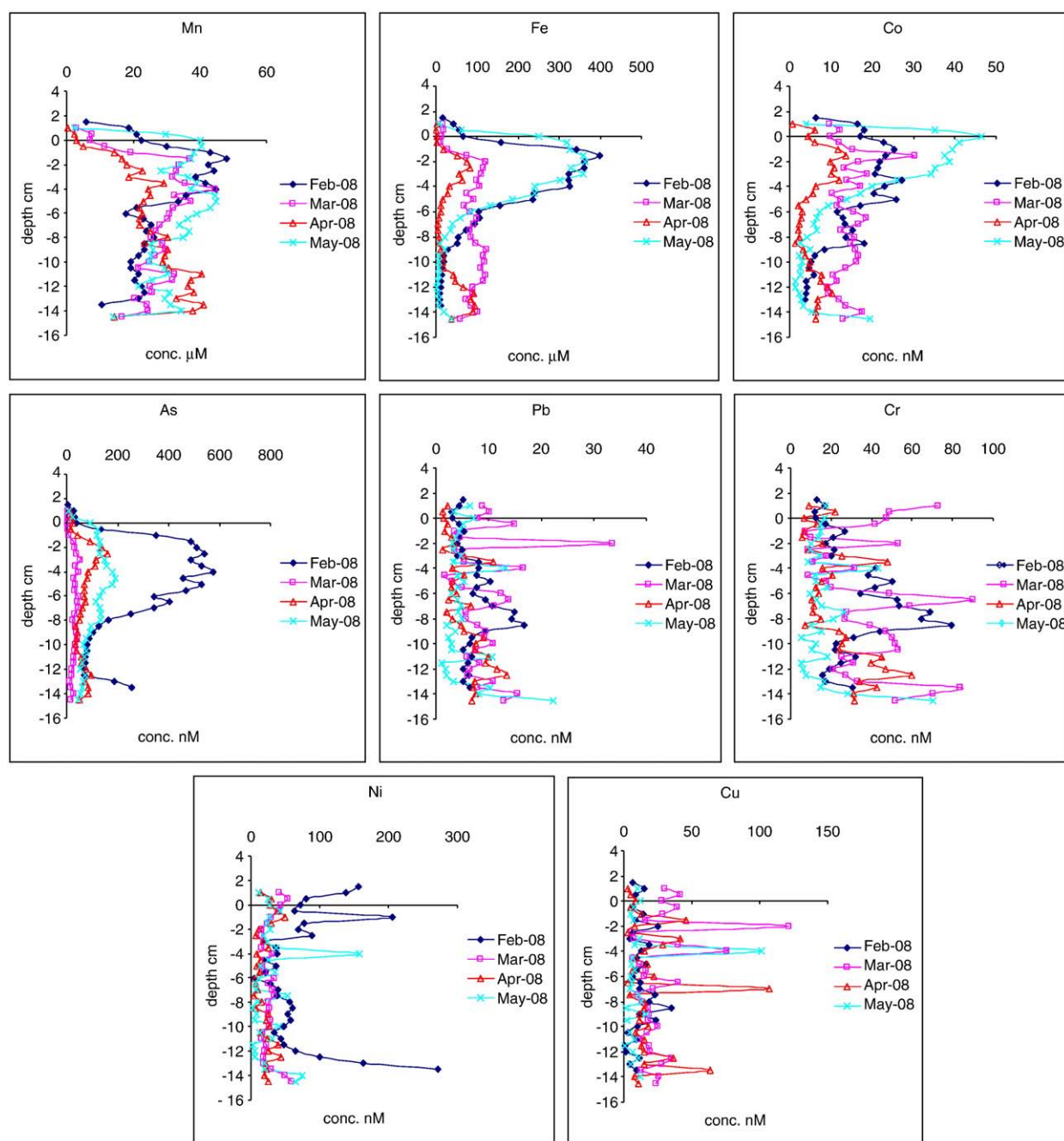
Fig. 5. Vertical profiles of Mn (A), Fe (B), Co (C), As (D), Pb (E), Cr (F), Ni (G) and Cu (H) assessed by DGT from February to May 2008.

Fe, Mn and several other trace metals may be due to dissolved sulfide being almost absent from the system. In contrast DET and DGT profiles for the months of February and May show low trace metal with high dissolved sulfide levels (Fe, Cu). It is interesting to compare the solubility product of iron sulfide compounds (FeS) reported in literature (Davison, 1991, Rickard and Morse, 2005) with our results. Iron sulfide solubility (pKs), decreases as follows in a marine system: amorphous ferrous sulfide with pKs of 2.95 ± 0.1, mackinawite of 3.6 ± 0.2, greigite of 4.4 ± 0.1, pyrrhotite of 5.25 ± 0.2 and pyrite of 16.4 ± 1.2 (Davison, 1991). The concentration levels of Fe^{2+}, dissolved sulfide and pH observed in our study are comparable to those reported by Davison (1980, 1991). It is absorbing that the solubility of FeS in a marine solution, >pH 7, is not well understood

(e.g. Rickard and Morse, 2005). Using the equations reported by Davison (1991), which define the ionic activity product (IAP),

$$IAP = \left[Fe^{2+}\right][HS^-]\gamma Fe^{2+}\,\gamma HS^-\left(H^+\right)^{-1} \tag{4}$$

$$K_1 = a[HS^-]a\left[H^+\right] / a[H_2S] \tag{5}$$

we attempted to predict the presence and the nature of FeS compounds. Eq. (5) was used to derive the concentration of HS^- from the total soluble sulfide, i.e. $H_2S + HS^-$ (S^{2-} being negligible) levels. Values of γFe^{2+} and γHS^- in seawater were taken from Davison (1980). In the case of high Fe^{2+} (about 700 µM for DET,

100 μM for DGT) and low dissolved sulfide concentrations (about 1.5 μM) (observed at 3–4 cm of depth in the month of February), the $-\log(\mathrm{IAP})$ values equal 2.83, by using DET values for Fe^{2+}, and 3.67, by using DGT values for Fe^{2+}, which are in the range of amorphous ferrous sulfide and mackinawite; in the case of low Fe^{2+} (about 70 μM for DET and 5 μM for DGT) and high dissolved sulfide concentrations (about 80 μM) (deeper sediment layers in the month of May), similar $-\log(\mathrm{IAP})$ values were obtained. The calculated $-\log(\mathrm{IAP})$ value based on the DET Fe concentrations is perhaps overestimated because not all DET Fe is labile. In order to corroborate the above findings, the Visual MINTEQ ver. 2.40b software was used to calculate the saturation index (SI) (Eq. (6)) of iron, manganese, arsenic, cobalt, copper and lead precipitates (Gustafsson, 1999).

$$\mathrm{SI} = \log(\mathrm{IAP} / K_s) \qquad (6)$$

For these calculations the following compounds have been taken into account: (1) cations, H^+, Ca^{2+}, K^+, Mg^{2+}, Na^+, Fe^{2+}, Mn^{2+}, As^{3+}, Co^{2+}, Cu^{2+}, Pb^{2+}; (2) anions, HCO_3^-, SO_4^{2-}, Cl^-, HS^- and (3) DOC, 50% are fulvic and 50% are humic acids. According to these calculations, FeS (amorphous) should not exist since SI values are always below 0. Conversely, troillite and pyrrhotite are oversaturated, implying that these compounds do not precipitate quickly in our sediments. Both iron sulfide minerals mackinawite and greigite are probably present in our sediments. By using DGT data, that are the best for this kind of calculations because only the labile fraction of iron is taken into account, greigite is slightly oversaturated whereas mackinawite is at equilibrium or slightly undersaturated. Finally, siderite ($FeCO_3$) may exist at some depths. MnS does not precipitate as a pure mineral; hence Mn should be incorporated into other labile sulfides like greigite and/or pyrite compounds. Conversely, $MnCO_3$ may exist as a pure mineral depending upon the season and the depths. Precipitation of As^{3+} does not occur in these pore waters, when sulfide concentrations are low in February (3–4 cm), H_3AsO_3 (98%) is the main prevailing species, while in the other case $AsS(OH)HS^-$ is the major species (>80%) leading to a possible explanation for high solution phase As^{3+} concentrations. Sulfides also control the concentration of Co through the CoS_a mineral where CoS_b is clearly oversaturated at $\log(\mathrm{SI}) > 4$ and therefore precipitates yet CoS_a, $-0.2 < \log(\mathrm{SI}) < 0.6$ is at solution equilibrium. Between 35 and 70% of Co is present as Co^{2+}. When sulfides are present, $CoHS^+$ is the abundant species (28–48%), carbonate and sulfate complexes represent about 30% in February (3–4 cm). DOC does not appear to have a significant effect on the labile species of As and Co.

Alternatively, labile Cu and Pb are less affected by sulfide and Cu is well known to be associated with organic matter. When sulfide concentrations are lower (February 3–4 cm), 96% of Cu is associated to phenolic groups of HA and FA, when sulfide concentrations are high, the complexation of Cu^{2+} with organic ligands is rather low (about 3–5%) and sulfide-copper minerals (covellite: CuS and chalcopyrite: $CuFeS_2$) are strongly oversaturated. When considering polysulfides rather than sulfides, covellite and chalcocite are still oversaturated with a log (SI) around 3 instead of >8 suggesting that polysulfides and

Table 2
Exchange fluxes of trace elements at the sediment water interface: calculated from vertical pore water profiles.

Element	Calculated flux in February (mmol·m^{-2}·d^{-1})	Calculated flux in April (mmol·m^{-2}·d^{-1})
Mn	0.10	0.063
Fe	1.6	0.26
Co	5.7E−05	4.2E−05
As	1.6E−03	4.4E−04
Cr	6.2E−05	0
Ni	−1.2E−03	1.6E−04
Cu	8.6E−05	5.4E−05
Pb	0	0

Table 3
Remobilization fluxes of trace elements at the sediment water interface in April, calculated from pore water profiles and estimated by DGT pistons.

Element	Calculated flux (mmol·m^{-2}·d^{-1})	DGT piston (mmol·m^{-2}·d^{-1})[a]
Mn	0.063	0.10
Fe	0.26	0.095
Co	4.2E−05	4.4E−05
As	4.4E−04	3.7E−04
Cr	0	2.8E−04
Ni	1.6E−04	3.0E−03
Cu	5.4E−05	9.5E−04
Pb	0	7.0E−05

[a] These values are average values obtained from three different deployment times: 2, 4 and 6 h in different sediment cores. For most elements, Relative Standard Deviation is about 100% due to sample heterogeneity.

may be S-organic compounds, may play a key role in the copper behaviour in these sediments. Several PbS solubility products have been proposed in the literature. In the Visual Minteq database logKs = -15.663 for the following reaction: $PbS + H^+ <=> HS^- + Pb^{2+}$. The mineral galena and PbS_{am} are oversaturated (log (SI) >3.4), except in the sample where the sulfide concentration is low and Pb is associated with organic ligands (about 70%). Fulvic acids (and more precisely phenolic groups) seem to be stronger ligands than humic acids.

The vertical profiles of Mn, Fe and As assessed by DET and DGT indicate that the remobilization zone and subsurface maximum of these elements shifts upwards, closer to the sediment water interface (SWI), advancing from February to May, corresponding with a decrease in oxygen concentrations and redox potential from winter to spring (Fig. 2).

3.3. Exchange fluxes of trace elements at the SWI

The DGT profiles of Mn, Fe, Co, As and Cu at station 130 in February and April (Cr only in February) show increasing concentrations with depth (Fig. 5). Ni presents a reversed trend in February, while Pb in February and April and Cr in April have more or less constant concentrations in the water column and pore water layers adjacent to the SWI (Fig. 5). We calculated concentration gradients and exchange fluxes over 2 cm of depth and as mentioned before in Section 3.2, for each element at the SWI using a diffusion coefficient of 10^{-5} cm^2 s^{-1} (Baeyens et al., 1986), which was corrected for a porosity value of 0.9 (the ratio of the fluid volume to the total volume of sediment). Exchange fluxes of trace metals in February maybe slightly higher due to diagenetic processes, than in April (Table 2). Oxygen and redox values as well as Fe and Mn concentrations are lower in April than in February. As suggested earlier in this paper, freshly produced organic matter (POM) entering the sediment pore waters can bind dissolved Fe and Mn compounds, reducing their pore water concentrations. Fe and Mn outfluxes (sediment to overlying water) are higher (0.063–1.6 mmol·m^{-2}·d^{-1}) compared to the other elements Co, As and Cu ($4.2 \cdot 10^{-5}$–$1.6 \cdot 10^{-3}$ mmol·m^{-2}·d^{-1}). Also the Ni influx in February is of the order of the outfluxes of the latter elements (Table 2). In suboxic conditions, similar iron and manganese fluxes across the SWI were reported by Pakhomova et al. (2007).

Remobilization fluxes of trace metals at the SWI, estimated by "DGT pistons", placed at the SWI, were used to calculate fluxes based upon the element concentration in the DGT resin and the DGT equation characteristics (see Eq. (3)). We estimated minimal fluxes with the assumption that all solutes moved with the speed of the free ions through the DGT gel layer, while metal complexes move slower (Zhang, 2004). The flux also corresponds to the trace element amount in the sediment that can be mobilized (including the labile fraction in the solid sediment phase) and that is further vertically transported up to the probe (Table 3). The "DGT piston" fluxes and the ones calculated via the concentration gradients for Mn, Fe, Co As are within the same

order of magnitude and Cr, Ni, Cu and Pb fluxes are at least 10 times greater. In fact from the DGT piston, acting as a "pump" at the SWI, trace element concentrations may be directly measured. The trace element concentrations at the SWI and the overlying water are zero (the "DGT piston" is placed at the SWI), thus maximizing the concentration gradient which is not always accomplished when the exchange fluxes are calculated based on the vertical concentration profiles. However, for Mn, Fe, Co and As both fluxes are rather similar which can be explained by the fact that in the overlying water their dissolved phase concentrations are very low as a result of rapid oxidation and precipitation.

Sediments are not closed environments, receiving inputs during the spring and summer recently produced particulate organic matter and associated elements and releasing afterwards a major part of this input in a dissolved form, according to the diagenetic processes taking place inside the sediment. In addition, particulate material of terrestrial origin will deposit year round in coastal sediments. Still it is interesting to calculate the half-life of the trace metals in the first 2 cm of the solid phase of the sediment using the outfluxes obtained with the "DGT pistons" and assuming it is a closed environment and outfluxes remain constant with time. Half-life amounts to: 0.33 y (Mn), 0.46 y (Ni), 0.65 y (Cu), 0.83 y (As), 5.3 y (Pb), 11 y (Cr and Fe). Hence, even without any supplementary input into those sediments, some trace metals will stay there for at least a decade.

4. Conclusion

Diagenetic processes at coastal station 130 in the surface sediment layers rich in organic matter and in contaminants control the pore water concentration and speciation of trace metals. Dissolved oxygen levels are highest both in overlying bottom waters and sediment pore waters during the months of February and March (at 0.3 cm of depth dissolved oxygen is exhausted) while in the spring months of April and May dissolved oxygen is completely consumed at sediment depth greater than 0.1 cm. Based on POC, $\delta^{13}C$ and $\delta^{15}N$, we can conclude that freshly produced POC was incorporated as bottom sediment in March and April, resulting in increased microbial activity and a reduction of the oxygen levels and therefore changing the sediment redox potential. Dissolved Mn, Fe and As DET profiles show a subsurface maximum and minimum at the detection limit in the deeper sediment layers.

The DGT profiles of Fe, Mn and As in the surface sediments are similar to those observed with the DET except for the March profile of Fe, which after an initial, suboxic increase remains almost constant over the whole depth of the core. Other trace metals: Co and Ni show suboxic maxima while the Pb and Cr profiles present several sporadic high levels at various depths. In deeper sediment layers dissolved sulfide clearly controls the dissolved trace metal contributions. In March dissolved sulfide is almost absent, resulting in higher Fe and Mn concentrations as demonstrated by the DET experiments. Also several other trace metals show higher labile dissolved levels in those sediment layers. During the months with high dissolved sulfide levels (February and May), DET and DGT trace metal concentrations are low.

Seasonal effects on trace metal profiles in the pore waters, by phytoplankton blooms (especially in the surface sediment layer) on the one hand and by sulfide (in the deeper sediment layer) on the other hand, were investigated. The phytoplankton biomass at station 130 was low until March (<1.5 µg chl-a L^{-1}), and then gradually increased to about 16 µg chl-a L^{-1} by mid April. When the pore waters became enriched in this newly supplied DOC (dissolved organic carbon)/POC (particulate organic carbon) in March–April, large Fe–organic complexes could be formed. Part of these large complexes are unable to diffuse into the small pores of the DET and DGT gels (Davison and Zhang, 1994; Zhang and Davison, 1999), and may explain the lower subsurface maximum of Fe in April (the same, but less pronounced is true for Mn and As). For labile dissolved Fe (DGT), this is also valid in March. In the deeper sediment layers, during

February and May sulfide levels are high and total dissolved Fe levels (DET) are low, while during the other months it is the reverse and Fe levels can be quite high, 340 µM. The seasonal variability of the Mn profiles (DET) is similar but much less pronounced than for Fe.

In order to better understand the observed vertical trace metal profiles in terms of sulfide, carbonate, organic matter and other ligands were also considered. The saturation index (SI) of Fe, Mn, As, Co, Cu and Pb compounds were calculated for low (the surface sediment layer in February) and high sulfide concentrations (the deeper sediment layer in May). According to these calculations, Fe and Co seem to be controlled by sulfides. Only when sulfide levels are high are Cu and Pb controlled and Mn and As not at all. Organic matter may also play an important role especially in the case of Cu and Pb. Copper is well known to be associated with organic matter, and when sulfide concentrations are weak (February 3–4 cm), 96% is associated to phenolic groups of HA and FA. In the other case, the complexation of Cu^{2+} with organic ligands is rather low (about 3–5%) and copper-sulfide minerals (covellite: CuS and chalcopyrite: $CuFeS_2$) are strongly oversaturated. When considering polysulfides rather than sulfides, covellite and chalcocite are still oversaturated but log (SI) is close to 3 instead of >8 suggesting that polysulfides and may be also S-organic compounds, may play a key role in the copper behaviour in these sediments. For Pb, the galena mineral and PbS_{am} are oversaturated (log (SI) >3.4), except in the sample where the sulfide concentration is low and Pb is associated with organic ligands (about 70%). Since all trace metals were enriched versus iron in the bulk surface sediments at station 130, adsorption to or co-precipitation with iron oxides or sulfides is certainly also a control mechanism of the dissolved trace metal levels in those surface sediments.

Exchange fluxes of trace metals (these are minimum fluxes) in February are slightly higher than in April. Fe and Mn outfluxes (sediment to overlying water) are higher than those of Co, As and Cu. The Ni influx in February is of the same order as the outfluxes of the latter elements. The "DGT piston" fluxes are of the same order of magnitude than the ones calculated via the concentration gradients at the SWI for Mn, Fe, Co and As, but at least 10 times higher for Cr, Ni, Cu and Pb. With the "DGT pistons", we directly measure in fact the sediment outflux because the trace metal concentration at the SWI is zero and hence the DGT acts as a "pump". We also found that for the redox sensitive elements such as Mn, Fe, Co and As that condition is also satisfied because the concentration at the SWI is also very low.

The sediments we studied can be classified as contaminated and what is their potential effect on the biodiversity? According to the background levels of trace metals in sediments in the North Sea reported by OSPAR (2000): Cu/Al (2.2–5.7 10^{-4}), Pb/Al (1.8–4.0 10^{-4}) and Cd/Al (0.007–0.030 10^{-4}), our values are equal to the upper value for Cu, are 2.5 times higher than the upper value for Pb and 5 times higher than the upper value for Cd. Preliminary and actually unpublished results indicate that in sediments near the Belgian coast (including station 130), a loss of biodiversity in Eubacteria is observed versus stations more offshore. One of the main factors we are currently investigating is the outflux of trace metals.

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