

## Response of diffusive equilibrium in thin films (DET) and diffusive gradients in thin films (DGT) trace metal profiles in sediments to phytodetritus mineralisation

Yue Gao,<sup>A,F</sup> Martine Leermakers,<sup>A</sup> Annelies Pedé,<sup>C</sup> Aurelie Magnier,<sup>A</sup> Koen Sabbe,<sup>C</sup> Beatriz Lourino Cabana,<sup>E</sup> Gabriel Billon,<sup>D</sup> Willy Baeyens<sup>A</sup> and David C. Gillan<sup>B,E</sup>

<sup>A</sup>Laboratory of Analytical and Environmental Chemistry (ANCH), Faculty of Science, Vrije Universiteit Brussel, Pleinlaan 2, B-1050 Brussels, Belgium.

<sup>B</sup>Laboratory of Proteomics and Microbiology, Faculty of Science, University of Mons, Avenue du Champ de Mars 6, B-7000 Mons, Belgium.

<sup>C</sup>Laboratory of Protistology and Aquatic Ecology, Faculty of Science, Ghent University, Krijgslaan 281 S8, B-9000 Ghent, Belgium.

<sup>D</sup>Laboratoire Géosystèmes, FRE 3298, Equipe Chimie et Sédiment, Université Lille 1, Avenue Paul Langevin, F-59655 Villeneuve d'Ascq, France.

<sup>E</sup>Laboratory of Marine Biology, Faculty of Science, Université Libre de Bruxelles, Avenue Franklin Roosevelt 50, B-1050 Brussels, Belgium.

<sup>F</sup>Corresponding author. Email address: yuegao@vub.ac.be

**Environmental context.** Contaminated sediments can have a large and lasting effect on marine ecosystems. It was discovered that significant amounts of pollutants, especially arsenic, were released from contaminated sediments during a phytoplankton bloom in the Belgian Continental Zone. Once released to the water column, these pollutants can accumulate up marine food chains and be a source of contaminants to humans.

**Abstract.** Field data from the Belgian Continental Zone showed elevated trace metal concentrations at the sediment–water interface after the occurrence of a phytoplankton bloom. In the present study, laboratory incubation experiments were used to investigate the effect of the phytodetritus remineralisation process on the release of trace metals from contaminated muddy sediments. This remineralisation process was followed by the measurement of chlorophyll-*a* and dissolved organic carbon levels in the top sediment layers. Two gel techniques, diffusive equilibrium in thin films (DET) and diffusive gradients in thin films (DGT), were used to assess vertical metal profiles in the sediment pore waters and to calculate the metal effluxes. These metal effluxes compared very well with the trace metal concentration variations in the overlying water of the sediment. Much higher effluxes of Mn, Co and As were observed after 2 days of incubation in the microcosms which received additions of phytodetritus. This trend gradually decreased after 7 days of incubation, suggesting that the elevated efflux of trace metals was proportional to the quantity of phytodetritus mineralised at the sediment–water interface. The release of large amounts of toxic elements from the sediments after phytoplankton blooms can therefore potentially affect the marine ecosystem in the Belgian Continental Zone.

**Additional keywords:** effluxes, incubation experiments, phytoplankton bloom.

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### Introduction

The Belgian Continental Zone (BCZ), 65 km (length of the coastline) × 31 km (offshore), is characterised by intense phytoplankton blooms resulting from the supply of continental nutrients into the BCZ.<sup>[1–3]</sup> Strong seasonal patterns are observed in the BCZ with diatom blooms initiating the flowering period in February–March followed by the main spring bloom composed of diatoms and *Phaeocystis globosa* in April–May.<sup>[4,5]</sup> Sedimentation of phytoplankton and phytodetritus represents a major source of organic matter (OM) for the benthic system where it fuels benthic life.<sup>[6,7]</sup> The benthic

response to phytoplankton sedimentation, including the fate of freshly deposited OM, differs between sediment types because it depends on the available amount of oxidants. Rapid degradation of OM often takes place in coarser, sandy sediments,<sup>[8]</sup> where dissolved oxygen penetration is much deeper. On the contrary, in fine-grained depositional areas, accumulation and sharp vertical gradients of OM build up after phytodetritus sedimentation in spring, whereas oxygen is rapidly exhausted, especially during and after phytoplankton blooms.<sup>[8]</sup> The degradation of OM by bacteria in sediments is coupled to the consumption of oxygen, nitrate, manganese and iron oxyhydroxide and sulfate

as the final electron acceptors before methanogenesis processes. The reduction of manganese and iron oxyhydroxide (solid phases) will result in the release of associated trace elements such as Co, Cu, Cd, Ni and Pb from the top sediment into the water column. A previous study<sup>[9]</sup> suggested that the remobilisation zone and subsurface maxima of Mn, Fe and As in the sediments at the Belgian coastal station 130 shifts progressively upwards, closer to the sediment–water interface (SWI), from February to May, corresponding with a decrease in oxygen concentrations and redox potential. As the oxygen penetration depth is small for muddy sediments (a few millimetres), severe anoxic conditions may rapidly develop during phytoplankton blooms.<sup>[9,10]</sup> This is a result of the small grain size of the sediments which limits transport in the porewater. There are only a few studies dealing with the effect of phytoplankton remineralisation on the release of trace metals from contaminated muddy sediments. This remineralisation can cause significant changes in the redox state of the benthic ecosystem, affecting the benthic microbial community structure and metal behaviour. In previous studies we suggested that OM deposition could influence metal effluxes across the SWI in the BCZ,<sup>[9]</sup> but further investigations considering both phytoplankton remineralisation and trace element mobilisation under controlled OM deposition conditions should be carried out.

Considering the initial in-situ conditions in aquatic sediments, especially at the SWI, diffusive equilibrium in thin films (DET)<sup>[11]</sup> and diffusive gradients in thin films (DGT)<sup>[12]</sup> are suitable sampling techniques. DET uses a gel that equilibrates with the bulk solution, hence with this technique no preconcentration is obtained, and compounds larger than the pore size are excluded. Mortimer et al.<sup>[13]</sup> and Fones et al.<sup>[14]</sup> used DET samplers for the determination of high spatial resolution profiles of solutes in marine or estuarine sediments. The DGT technique is based on the mass transport control of metals and is used in the water column and sediment porewaters. It utilises two hydrogel layers: a polyacrylamide gel covered with a membrane (0.45 µm) is usually used as the diffusive layer, and is backed up by a second binding layer containing for example a Chelex cation-exchange resin selective for metals. With this technique, only the metal fraction small enough to diffuse through the gel, dissociating fast enough in the gel and capable of binding to the resin layer is assessed. Applying Fick's diffusion law, the fluxes of the labile metal fraction into the DGT probe can be calculated. DGT probes have been inserted vertically in sediment porewaters in several studies to determine high-resolution profiles of trace elements.<sup>[15–19]</sup>

The goal of the present study is the application of DET and DGT techniques in sediments loaded by fresh phytodetritus and placed in small microcosms: (1) to study the geochemical behaviour of trace metals at the SWI and (2) to determine the efflux of trace metals from the sediment to overlying water. With these results we will gain new insight into the role played by surficial sediments in the BCZ in trace metal release or scavenging during the period of phytoplankton bloom.

## Experimental

### Sediment collection

Integral sediment samples were collected at Belgian coastal station 130 (51°16.25'N, 02°54.30'E) with a Reineck corer (diameter = 15 cm) in March 2010. Sediments were immediately transferred into 18 cylindrical plexiglass microcosms (15-cm diameter, 16-cm length) with 4 cm of overlying seawater.

All microcosms were subsequently transported to the laboratory and stabilised for 10 days in the dark at  $15.0 \pm 1^\circ\text{C}$ .

### Algal cultures and algal suspension

In this study, *Phaeocystis globosa* and *Skeletonema costatum*, which are important species involved in the phytoplankton blooms in the BCZ, were cultivated in medium F20, which is a mixture of major nutrients, trace metals, minor elements and vitamins added to seawater.<sup>[20]</sup> Natural seawater was filtered through a 0.2-µm Sartorius membrane and autoclaved for 20 min at  $121^\circ\text{C}$  before use. Cultures were grown at  $9\text{--}10^\circ\text{C}$  under an irradiance of  $100\ \mu\text{E m}^{-2}\text{ s}^{-1}$  and a gentle agitation of the culture flasks, and then they were decanted, centrifuged and stored deep-frozen. One day before the experiment, the deep-frozen cell pellets were thawed and suspended in 8 L of natural seawater. This algal suspension was used for the algal incubation experiments. The proportion of the two algae species in the algal suspension was 50 : 50 (w/w), the total chlorophyll-*a* content was  $750 \pm 35\ \mu\text{g L}^{-1}$  (mean  $\pm$  s.d.), and the salinity 30. The biomass of the algal suspension was  $131\ \text{mg L}^{-1}$  (dry weight, DW), measured after centrifugation and lyophilisation of three 50-mL samples).

### Experimental design

The overlying sea water in all 18 microcosms was slowly removed in order to preserve the natural state of the SWI as much as possible. The 18 microcosms were then divided into two groups: to the first nine microcosms, 710 mL of algal suspension was slowly added (OMcosms), whereas the remaining nine received 710 mL of natural seawater (Blcosms). After 2 h, the measurements (in triplicate) of microbial and geochemical parameters (see next section) were started. The same measurements were repeated after 2 and 7 days. Salinity was monitored by a salinometer and kept constant by controlled additions of MilliQ water (Millipore,  $>18\ \text{M}\Omega$ ). The experiment was carried out at a temperature of  $15 \pm 1^\circ\text{C}$ , which is the natural temperature in the BCZ during a phytoplankton bloom.

### Geochemical parameters

Dissolved oxygen concentration was measured in the overlying water, chlorophyll-*a* and dissolved organic carbon (DOC) concentrations were determined at the SWI and redox potential (Eh) and pH profiles in the sediment porewater were also determined.

The dissolved oxygen in the overlying water was measured at 5 mm above the SWI using a WTW CelloX 325 galvanic oxygen sensor (VWR, France) adapted for measurements in seawater. Eh and pH measurements were performed using a combined redox electrode with an Ag/AgCl ( $[\text{KCl}] = 3\ \text{M}$ ) reference electrode and a pH combined electrode. All potential values reported herein are expressed against the Ag–AgCl electrode. The pH electrode is calibrated with Merck buffers, type NBS (National Bureau of Standards) and Eh electrode with redox calibrating solution (220 mV Pt–Ag/AgCl, 3 M KCl, WTW). In addition, as measurements were carried out in seawater, a correction of the values was made according to Aminot and K  rouel.<sup>[21]</sup>

The frozen surface sediment samples were lyophilised for chlorophyll-*a* analysis. The pigments were extracted in 90 % acetone and analysed using HPLC according to standard protocols.<sup>[22]</sup> Chlorophyll-*a* concentrations were expressed as micrograms per gram of sediment (DW). For DOC analysis, all glassware and filters were previously treated at  $500^\circ\text{C}$  for 4 h.

Surface sediment porewaters were centrifuged and collected through Whatman GF/F glass fibre filters (VWR, Belgium) and preserved with 5 % of phosphoric acid at 4 °C. A Dohrmann Apollo 9000 total organic carbon analyser (Teledyne Tekmar, Mason, OH, USA) was used for DOC concentration measurement.

Metals in the overlying seawater were assessed by high-resolution inductively coupled plasma–mass spectrometry (HR-ICP-MS, Thermo Finnigan Element II, Thermo, Bremen, Germany) after passing through a 0.45- $\mu\text{m}$  cellulose filter, and total dissolved metals in porewaters were determined by DET and metal fluxes by DGT sampling. DET and DGT probes were prepared in the laboratory according to the protocol reported by Gao et al.<sup>[9]</sup> An agarose-polyacrylamide hydrogel consisting of 15 % acrylamide (Merck, Belgium) and 0.3 % agarose-derived crosslinker (DGT Research Ltd, UK) was used as a diffusive gel. Ion exchange resin (Chelex 100, Biorad, Germany) with a bead size of 200–400 mesh (Biorad) was used as the binding agent. Before deployment, DET and DGT probes were de-oxygenated in artificial sea water with reduced trace metal concentration (5–10 g of Chelex 100 were added to remove trace metals).<sup>[17]</sup> After preparation of the Blcosms and OMcosms (see above for definitions), the DET and DGT probes were deployed in these microcosms at the following time periods for 24 h: Day 0–1, Day 2–3 and Day 7–8. After the incubation experiment, 75 slices of DET gels were transferred into pre-weighed polypropylene vessels and eluted with 1 mL of 1 M  $\text{HNO}_3$  solution, whereas the resin gels inside the DGT probes were cut into 5-mm slices and eluted with 1 mL of 1 M  $\text{HNO}_3$  solution. All gel solutions were analysed by HR-ICP-MS.

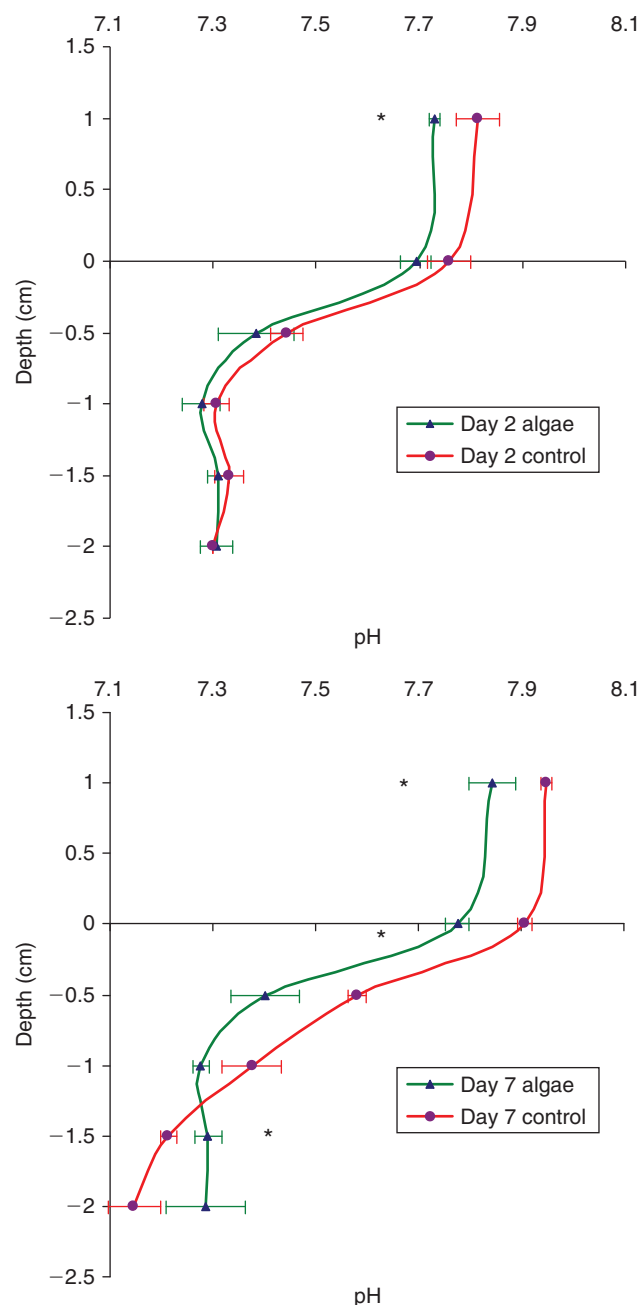
## Results and discussion

### *pH and Eh profiles at the SWI*

The SWI in the OMcosms was slightly acidified compared with that in the Blcosms on Day 2 and Day 7 (Fig. 1). According to a previous study,<sup>[23]</sup> mineralisation of OM by bacteria in anoxic conditions decreased the pH in the upper sediment layer. Also the Eh values in the first centimetre below the SWI decreased faster in the OMcosms on Day 2 and Day 7, reaching a value of 0 mV (v. Ag–AgCl) within the first centimetre of the sediments (Fig. 2). Moreover, the Eh profiles on Day 2 reached a value of 0 mV faster than on Day 7. On the contrary, in the Blcosms, the Eh profiles increased slightly just below the SWI on Day 2 and Day 7 but decreased from 0.5 cm to achieve a value of 0 mV below 1 cm of sediment depth. Redox profiles in the Blcosms on Days 2 and 7 were similar. Oxygen levels, measured at 5 mm above the SWI, varied between 4 and 6  $\text{mg L}^{-1}$  throughout the experiment with a slightly higher concentration in the Blcosms than in the OMcosms. Salinity was stable, with values of  $30.0 \pm 0.5$  in all microcosms.

### *Chlorophyll-a and DOC concentrations at the SWI*

The chlorophyll-a content was measured at the SWI (Fig. 3). All sediment cores presented a background chlorophyll-a concentration of  $\sim 20 \mu\text{g g}^{-1}$  (DW). The introduction of phytodetritus into the OMcosms was clearly visible; 2 h after the addition, values of chlorophyll-a significantly increased from 20 to 30  $\mu\text{g g}^{-1}$ . After 2 and 7 days, chlorophyll-a values were 42 and 35  $\mu\text{g g}^{-1}$  in the OMcosms, whereas a value of  $\sim 20 \mu\text{g g}^{-1}$  was maintained in the Blcosms. Values of DOC in the 0–5-mm porewaters are shown in Table 1. The mean DOC values of the OMcosms increased with the incubation time, which is clearly

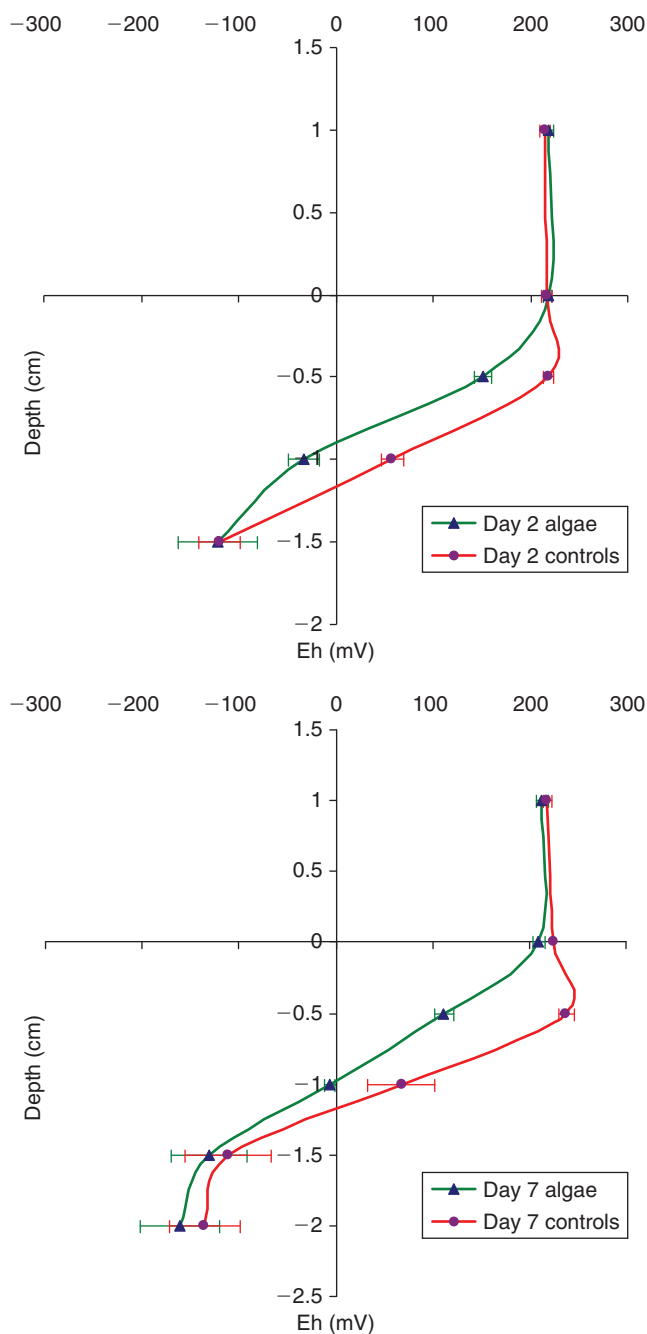


**Fig. 1.** pH profiles during the microcosm incubation experiments: with addition of algae (OMcosms) and without (Blcosms, control) (mean  $\pm$  s.d.,  $n=3$ ). Asterisks (\*) indicate significant differences (student's *t*-test,  $P=0.05$ ).

indicative of a decomposition process, and no significant differences were found in the Blcosms for Day 0 and Day 7.

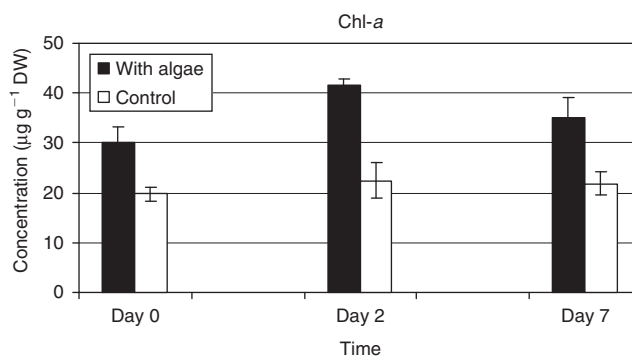
### *Metal concentrations in the overlying water*

Metals in the overlying waters were determined by HR-ICP-MS throughout the experiment. After 2 h of exposure to the algal suspension a significant increase of the metal concentrations in the overlying water was observed for Cd ( $0.46 \mu\text{g L}^{-1}$ ), Co ( $0.23 \mu\text{g L}^{-1}$ ) and As ( $2.5 \mu\text{g L}^{-1}$ ) in the OMcosms compared with the Blcosms (Cd ( $0.11 \mu\text{g L}^{-1}$ ), Co ( $0.12 \mu\text{g L}^{-1}$ ) and As ( $1.6 \mu\text{g L}^{-1}$ )). We first examined the possibility that this increase could result from addition of the algal culture solution.



**Fig. 2.** Redox potential (Eh) profiles during the microcosm incubation experiments: with addition of algae (OMcosms) and without (Blcosms, control) (mean  $\pm$  s.d.,  $n = 3$ ) (student's  $t$ -test,  $P = 0.05$ ).

Dissolved metal concentrations of the algal suspension (after  $0.45\mu\text{m}$  filtration) were as follows: Cd ( $0.71\mu\text{g L}^{-1}$ ), Co ( $0.28\mu\text{g L}^{-1}$ ) and As ( $2.8\mu\text{g L}^{-1}$ ). Hence, it could be easily demonstrated that the observed metal elevation after 2 h of exposure was directly related to the algal culture containing metals and not to any biogeochemical process. After 2 days of exposure (Day 2) the concentrations of four metals were significantly higher in the overlying waters of the OMcosms compared with those of the Blcosms: Cd ( $2.7\times$ ), Co ( $6.6\times$ ), Mn ( $12.7\times$ ) and As ( $2.2\times$ ). When calculating metal amounts originating from the algal culture it was easy to show that they were negligible compared with the high metal concentrations



**Fig. 3.** Chlorophyll-*a* (Chl-*a*) concentrations in the top sediment layer: with addition of algae (OMcosms) and without (Blcosms, control) (mean  $\pm$  s.d.,  $n = 3$ ).

**Table 1.** Dissolved organic carbon (DOC) (mean  $\pm$  s.d.,  $n = 3$ ;  $\text{mg L}^{-1}$ ) in the top sediment layer (0.5 mm)

The differences between samples with addition of algae (OMcosms) and without (Blcosms) are significant for the three sampling times (student's  $t$ -test,  $P = 0.05$ )

Sample	Sampling time		
	2 h	Day 2	Day 7
Control (Blcosms)	$14.3 \pm 5.2$	$14.6 \pm 2.8$	$17.2 \pm 1.3$
Algae (OMcosms)	$16.8 \pm 0.5$	$18.1 \pm 1.5$	$24.1 \pm 5.4$

observed in the overlying water of the OMcosms at Day 2. In the overlying waters of the Blcosms and OMcosms, less difference was observed between the trace metal concentrations at Day 7.

#### *Trace metal mobilisation in the surface sediment layer with and without phytodetritus addition*

As discussed in the previous section, trace metal levels in the overlying waters very quickly reflect the mineralisation process of phytodetritus deposits, and trace metals in the sediment porewaters and particularly in the top sediment layer also reflect phytodetritus addition. As a result of the high blank values of agarose used in the DET technique, only Mn, Co, Fe and As profiles could be measured. The Mn and Co DET concentration profiles increased by a factor of  $\sim 2$  in the OMcosms' sediments compared with that of the Blcosms after 24 h of exposure (Day 0–1 in Fig. 4). These metal concentrations rose very quickly in the top sediment layer after phytodetritus addition and the release is associated with an increase of the DOC concentration resulting from OM degradation in the sediments (Table 1). After 72 h of exposure (Day 2–3 in Fig. 4), Mn and Co concentrations in the OMcosms' sediments were higher than in the sediment of the Blcosms, but after 8 days (Day 7–8 in Fig. 4), concentration levels of both elements decreased again to the levels in the Blcosms' sediments. In contrast, Fe and As concentrations in the OMcosms' sediments were only higher than in sediment of the Blcosms after 8 days at the top sediment layer.

There are two possible sources for the elevated metal levels observed in the overlying water and in the sediment porewaters of the top sediment layer: (1) degradation of OM and subsequent release of metals bound to this OM and (2) reduction and subsequent dissolution of Mn and Fe oxyhydroxides related to OM degradation and release of metals associated with the oxyhydroxides. Manganese and cobalt concentrations showed



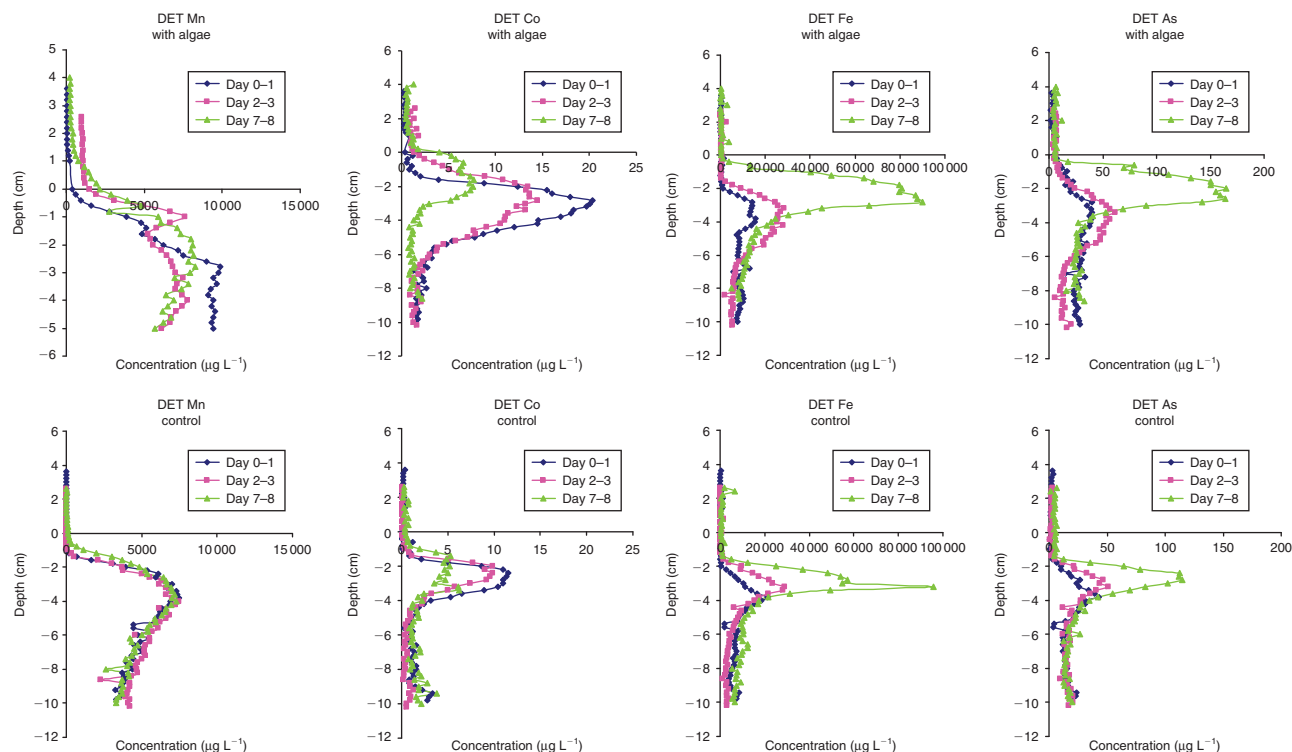


Fig. 4. Mo, Co, Fe and As diffusive equilibrium in thin films (DET) profiles in sediments.

an increasing trend in the overlying water from deposition of phytodetritus in the SWI but decreased again after 7 days of exposure, suggesting that the single phytodetritus deposition on the sediment was completely decomposed after 7 days. The lower chlorophyll-*a* level observed in OMcosms sediments after 7 days, confirms this phenomenon as discussed in the previous paragraph (Fig. 3). In a real marine system such as the BCZ, phytodetritus deposition to the sediments will start from the beginning of March (start of the phytoplankton bloom) and last until the middle of May (end of that bloom). Therefore, in a sediment continuously receiving phytodetritus, a continuous degradation of OM deposits will occur in the top layer. Consequently, enhanced metal concentrations in the surface sediment layer as well as in the overlying water will be observed for more than 2 months. This phenomenon has also been observed in the past<sup>[9]</sup> by our research group in the BCZ. However, iron did not display any trend in the overlying water, neither with nor without addition of phytodetritus, as a function of time. This is not surprising because reoxidation of dissolved Fe<sup>II</sup> in the overlying waters occurs in only a few minutes, immediately followed by precipitation of Fe<sup>III</sup> hydroxides. In the case of As, the addition of OM leads to the reduction of iron hydroxides in the surficial sediments and the release of As into the water column, as clearly observed on Day 7 in the OMcosms. Another specific feature of Fe and As is that the reduction zone appearing at 2–4-cm depth below the SWI for the Blcosms moved up closer to the SWI in the OMcosms after 7 days of exposure. This also happened with the Eh profiles at Days 2 and 7 in the OMcosms, reflecting a much stronger reduction environment in the latter microcosms compared with the Blcosms. Similar observations were made during the monthly campaigns in 2008 in the BCZ.<sup>[9]</sup>

Different from the DET technique, DGT can be considered as an integrating tool to determine metal fluxes from sediments to

the porewaters during the deployment time.<sup>[16]</sup> Cd, Ni, Mn and Co DGT profiles in the top sediment layer in the OMcosms showed an obvious increasing trend during the first 24 h, but the difference between the profiles in the OMcosms and the Blcosms became very small after 2 days of exposure (Fig. 5). There was no significant difference ( $P > 0.05$ ) between the Cd and Co profiles in the OMcosms and the Blcosms. However, the concentrations of Ni and Mn were significantly lower in the OMcosms (the same is true for Fe and As, data not shown). A possible explanation for the latter observation is that labile Ni and Mn pools in porewaters and the solid phase became more quickly depleted than Cd and Co.

The effluxes of several metals based on their concentrations in the overlying water were compared with those calculated based on DET profiles in the OMcosms. As the metal concentrations in the overlying water in the Blcosms hardly changed during the 7 days of experiment, it is not interesting to calculate their sediment effluxes. For example, Mn, Co and As concentrations observed after 2 days of exposure in the OMcosms were chosen for comparison. The phytoplankton culture has already been excluded as a possible source of the excess metal amount in the overlying water, thus this excess should result from sediment effluxes related to OM degradation. First effluxes based on the increase of the metal concentrations ( $C$ ) in the overlying water after 2 days of exposure were calculated. The volume of the overlying water is 710 mL, the surface area of the sediment in the microcosm is 176.62 cm<sup>2</sup> and the time period is 172 800 s. The efflux then equals:  $F = C \times V / (A \times T)$ , where  $F$ , metal fluxes;  $V$ , volume of water;  $A$ , passing area; and  $T$ , time period. On the other hand, we calculated metal concentration gradients and exchange fluxes based on DET profiles at the SWI for each of the elements using a diffusion coefficient of  $10^{-5}$  cm<sup>2</sup> s<sup>-1</sup>.<sup>[9]</sup> Comparable fluxes were obtained for Mn and As, whereas a slight difference was observed for Co, but the values were still of

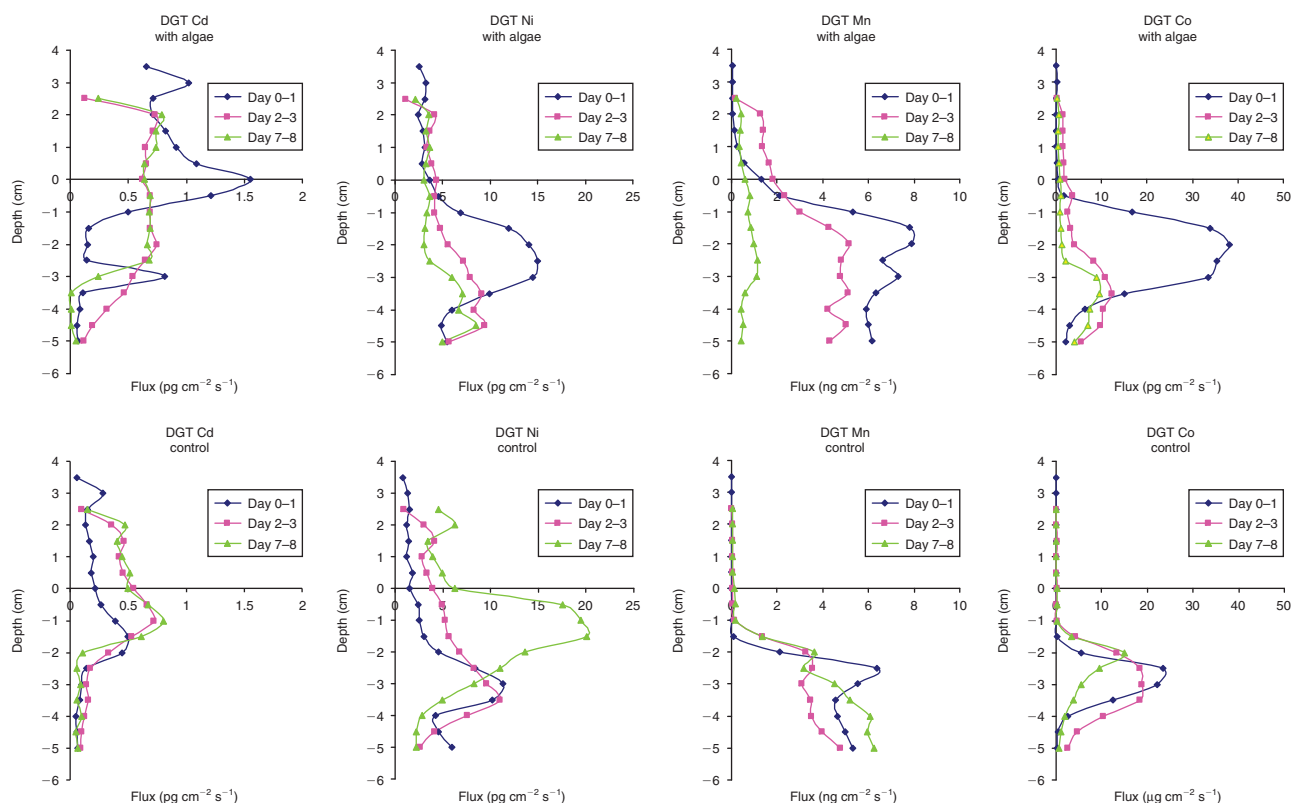


Fig. 5. Ni, Cd, Mn and Co diffusive gradients in thin films (DGT) profiles in sediments.

**Table 2.** Mn, Co and As sediment effluxes after algae addition

Relative standard deviation is  $\sim 100\%$  because of sediment heterogeneity

Elements	Fluxes based on overlying water concentration ( $\text{mmol m}^{-2} \text{day}^{-1}$ )	Fluxes based on diffusive equilibrium in thin films (DET) profiles ( $\text{mmol m}^{-2} \text{day}^{-1}$ )
Mn	0.30	0.39
Co	$2.28 \times 10^{-4}$	$6.13 \times 10^{-4}$
As	$7.02 \times 10^{-4}$	$7.43 \times 10^{-4}$

the same order of magnitude (Table 2). In contrast to Mn and Co, As is a carcinogenic element and may also accumulate along the food chain in the marine system. Fortunately As accumulated in fish is mainly transformed into arsenobetaine (more than 95% of total As in fish of the BCZ), an arsenic form that is not or only slightly toxic.<sup>[24]</sup> According to our calculation,  $\sim 7 \times 10^{-4} \text{ mmol m}^{-2} \text{day}^{-1}$  of arsenic will be released from sediments to overlying water in the coastal area of the BCZ during the period of phytoplankton bloom. If a surface area of  $720 \text{ km}^2$  is assumed for muddy coastal stations in the BCZ<sup>[25]</sup> and As is taken as an example, 0.24 t of arsenic can diffuse out of the sediments within the 2 months covering the phytoplankton bloom period and assuming a closed environment. Such huge amounts of arsenic will be distributed along the BCZ, accumulated by phytoplankton and microzooplankton, and further along the food chain by fish. High concentrations of total As were found in North Sea fish, with the highest amounts in lemon sole, dogfish, ray and witch.<sup>[24]</sup> Average total As concentrations in these fish species were higher than  $20 \text{ mg kg}^{-1}$  wet weight (WW). Fortunately, the toxic As fraction seldom exceeded 2%

of the total As concentration. Efflux calculations based on the DET profiles were an order of magnitude higher than those based on the DGT profiles obtained in April 2008,<sup>[9]</sup> confirming the DGT technique measures only a small fraction, i.e. the labile one, of that measured by the DET technique.

## Conclusion

Trace metal mobilisation in contaminated marine sediments is directly influenced by phytodetritus deposits. We have studied this process in microcosms containing sediments of the BCZ: to half of the microcosms an algal culture is added (OMcosms), the other half are used as control microcosms (Blcosms). The highest levels of trace metals in the overlying water appeared after 2 days of exposure: the concentrations of Mn, Co and As in the OMcosms were 12.7, 6.6 and 2.2 times higher than the values observed in the Blcosms.

As the culture was not the main source of these increased metal levels, they must be attributed to metal release from the top sediment layer associated with phytodetritus degradation. Effectively, in the OMcosms, the trace metal effluxes from the sediments to the overlying water, calculated based on DET profiles, are very close to those based on direct concentration measurements in the overlying water. During the period of the degradation, the pH and Eh were also modified and this resulted in further trace metal mobilisation in the upper sediment layer and effluxes to the overlying water. The chlorophyll-*a* concentration in the top sediment layer also showed its most elevated level after 2 days of exposure. However, these high chlorophyll levels are not directly linked with DOC levels in the top sediment layer; only several days later a DOC increase is observed. The upward and downward trend of chlorophyll-*a*, DOC and metal concentrations in the OMcosms reflect the

transient degradation and mineralisation of OM in a short time period, depending on the amount of phytodetritus deposited at the SWI. As mentioned above, in a real marine system such as the BCZ, phytodetritus deposition to sediments will start from the beginning of March and last until the middle of May covering the whole phytoplankton spring bloom period. This will result in a continuous OM degradation in the top sediment layer and consequently enhanced metal concentrations at the SWI in the BCZ over several months.

The present experiments demonstrated, at least for the phytoplankton bloom period, a high potential for metal remobilisation from sediments to overlying water. Future work should focus on sediment release of As in the BCZ and on its effect on benthic fauna.

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