



ELSEVIER

Marine Geology 182 (2002) 373–387



www.elsevier.com/locate/margeo

Fast-growing, shallow-water ferro-manganese nodules from the western Baltic Sea: origin and modes of trace element incorporation

S. Hlawatsch^{a,*}, T. Neumann^b, C.M.G. van den Berg^c, M. Kersten^d,
J. Harff^e, E. Suess^f

^a *Institute for Science Education, Ohlshausenstrasse 62, D-24098 Kiel, Germany*

^b *Institute for Petrography and Geochemistry, University Karlsruhe, D-76128 Karlsruhe, Germany*

^c *Oceanography Laboratories, University Liverpool, Liverpool L69 3BX, UK*

^d *Geoscience Institute, Gutenberg University, Becherweg 21, D-55099 Mainz, Germany*

^e *Baltic Sea Research Institute, Seestrasse 15, D-18119 Rostock, Germany*

^f *GEOMAR Research Center, Wischhofstrasse 1–3, D-24148 Kiel, Germany*

Received 24 May 2000; accepted 10 August 2001

Abstract

Ferro-manganese nodules of the western Baltic Sea reveal enhanced heavy metal concentrations since the end of the 19th century and are therefore potentially useful for retrospective monitoring of the heavy metal pollution history. However, only Zn shows a significant rise, even though Cu is also introduced to the western Baltic Sea by natural and anthropogenic sources. This study focused on geochemical considerations to evaluate the mechanism responsible for the predominance of Zn in ferro-manganese nodules compared to Cu. The particulate and dissolved metal fractions in the water column, in the fluffy layer (an approximately 2-cm-thick sediment layer situated at the sediment–water interface) and in the pore water adjacent to ferro-manganese nodules were studied. The analysis of the dissolved fraction and speciation studies were carried out using cathodic stripping voltammetry (CSV). The particulate fraction and the pore water were analyzed via graphite furnace–atomic absorption spectroscopy (GF–AAS) and inductively coupled plasma–optical emission spectroscopy (ICP–OES). The fluffy layer provides high quantities of Mn, Fe, Zn, and Cu to the dissolved fraction of the bottom water during the stratification period. Hence, the signal manifested in the ferro-manganese nodules consists of newly emitted elements on top of the amount collected in the fluffy layer over many years and remobilized throughout the stratification. Trace elements with the tendency to form weak inorganic complexes in the water column, like Zn, are more likely to be incorporated in ferro-manganese nodules and therewith document the anthropogenic metal input, while elements which tend to form strong organic complexes such as Cu are scavenged by particulate organic matter in the water column and the fluffy layer. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Baltic Sea; ferro-manganese nodules; zinc; copper; anthropogenic input; trace elements

* Corresponding author. Tel.: +49-431-880-3131; Fax: +49-431-880-2633.

E-mail address: hlawatsch@ipn.uni-kiel.de (S. Hlawatsch).

1. Introduction

Ferro-manganese nodules from the Baltic Sea consist of alternating Mn- and Fe-(hydr)oxide (Mn-oxides, Fe-oxyhydroxides, Fe-hydroxide) layers around a central core. While the (hydr)oxides accumulate, they incorporate trace elements from the water column (e.g. Winterhalter and Siivola, 1967; Boström et al., 1982; Ingri and Pontér, 1987; Heuser, 1988). Thus the analysis of a profile perpendicular to the direction of growth allows a chronological reconstruction of the trace element concentration in the seawater of the western Baltic Sea. Because of their growth rate of $0.02 \pm 0.002 \text{ mm yr}^{-1}$, fast-growing shallow-water ferro-manganese nodules from the western Baltic Sea cover the period since industrialization around 1840 (Hlawatsch, 1999).

The origin of ferro-manganese nodules is closely related to the biogeochemical cycling of Mn and Fe induced by redox conditions, which is described in detail for lake environments (e.g. De Vitre et al., 1988; Davison, 1993) and for Baltic Sea ferro-manganese nodules (Glasby et al., 1997). The western Baltic Sea favors the formation of ferro-manganese nodules because of the seasonal thermohaline stratification, which establishes during summer from June to September. The stratification reduces the oxygen exchange between the surface and the bottom water. Hence, any microbial decay of organic matter will result in oxygen depletion in the latter. Denitrification, manganese reduction, iron reduction and sulfate reduction (Froelich et al., 1979; Berner, 1980; Berner, 1981) occur successively in the bottom water of the western Baltic Sea while stratification gradually stabilizes (Harms, 1996). This contrasts to the deep-sea sediment where these processes take place simultaneously at different depths. The different redox potentials of the $\text{Mn}^{2+}/\text{Mn}^{4+}$ and the $\text{Fe}^{2+}/\text{Fe}^{3+}$ redox pairs (Davison, 1993) lead to delayed dissolution of Fe compared to Mn and the precipitation of Fe before Mn. Due to autumn storms, the water column is mixed and oxygenated again and Mn and Fe precipitate around particles or form a new layer on the ferro-manganese nodules (e.g. Djafari, 1976; Heuser, 1988; Hlawatsch, 1999). This process can be mi-

crobiologically mediated (Nealson, 1978; Ghiorse, 1980, 1982; Lovely, 1987; Nealson et al., 1988; Mandernak et al., 1995).

Of the trace elements, Zn shows the most significant enrichment, with a surface portion enrichment at least 6 times higher compared to the center. Co rises up to three times and As shows a slight enrichment. Cu and Cd with varying concentrations show no enrichment in the surface portion (Hlawatsch, 1999). Therefore we sampled the particles, the fluffy layer (which covers the ferro-manganese nodules) and the pore water to study the adsorption and desorption of Zn and Cu onto particles as well as their complexation in the water column. The aim was to clarify the mechanisms, which are responsible for the predominance of Zn in the nodules compared to other trace elements.

2. Materials and methods

2.1. Sample location and sampling

In July 1994 and September 1995, the Blinkerhügel area in the western Baltic Sea (Figs. 1 and 2) was visited with the research vessel *Prof. A. Penck*. The sediment distribution of the Blinkerhügel area was evaluated via echo-sounding (DESO 25). On-line underwater photograph- and video-techniques were applied to view and document the distribution of ferro-manganese nodules.

Water samples were taken in July 1994 from sites 4, 8 and 9 (Fig. 2) at three depths overlying the studied ferro-manganese nodules, using a sampling device combined with on-line detection of conductivity (for salinity) and temperature (OM 87). An additional water sample was taken at each site 40 cm above the seafloor, by a diver using a common Go-Flow water-sampling device. Sediments were sampled using a Rumohrлот gravity corer. This corer sampled bottom water, an undisturbed surface sediment layer, and up to 500 mm of underlying sediment. Sediment cores within the liners were transferred into an argon-flushed glove box to prevent oxidation, extruded and sliced into 10- to 20-mm discs. Sub-samples

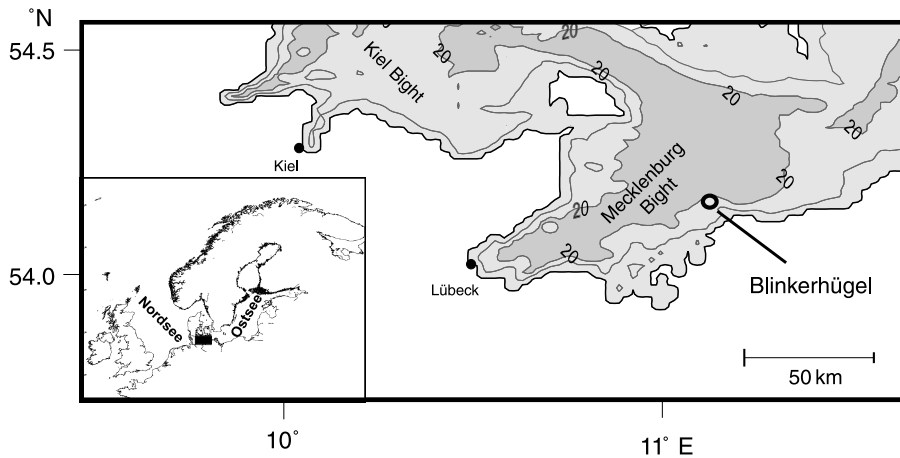


Fig. 1. Study area in the western Baltic Sea.

for bulk analyses were stored in polyethylene bottles and frozen. Pore waters were taken immediately after retrieval. The slices were transferred within the glove box in pre-cleaned polyethylene centrifuge bottles. After centrifuging, the supernatant water was filtered through 0.45- μ m nucleopore filters. Aliquots were used to determine sul-

fate and chlorite by ion chromatography. Subsamples of pore water were acidified with suprapure HNO_3 and kept frozen until analysis in the laboratory.

In September 1995, the same sites were re-sampled from a small boat (dinghy). At this time, instead of the sediment samples of the 2-

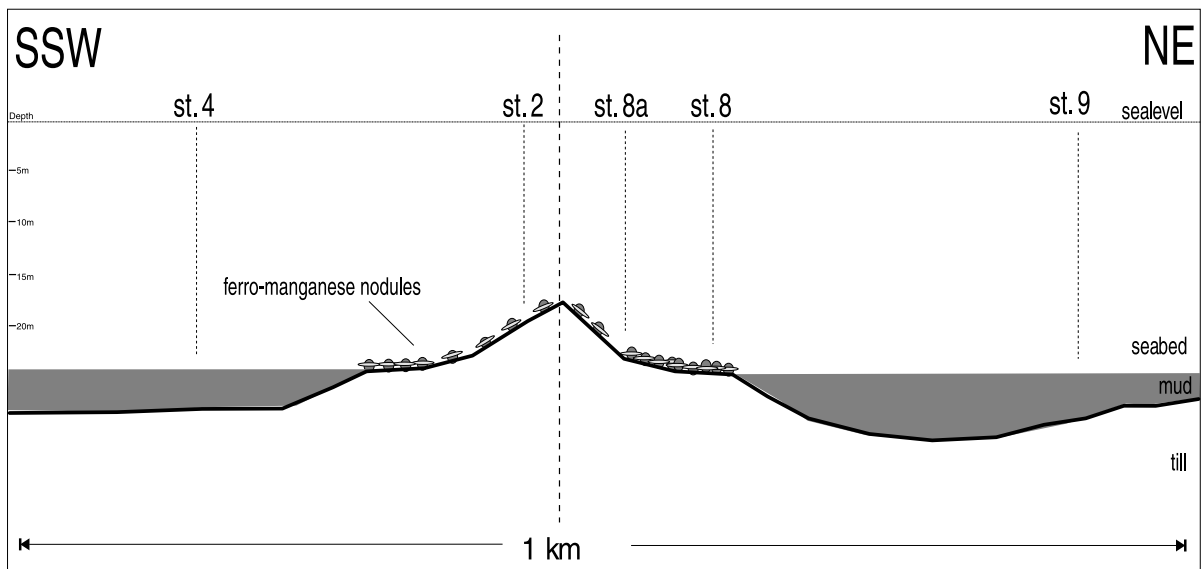


Fig. 2. Position of the sampled stations at the Blinkerhügel (interpreted after echo-sounding data).

cm-thick fluffy layer situated at the sediment–water interface, were taken by divers which introduced a small pipe of 0.5 cm diameter of a Mercos hand water-sampling device directly into the fluffy layer. Immediately after retrieval, the oxygen concentrations of sub-samples were determined using the Winkler method (Grasshoff et al., 1983). The fluffy layer samples were centrifuged and filtered in an argon-filled glove-box. Temperature, Eh, pH, pH_2S , and alkalinity were determined on sub-samples in the glove-box with a pH-meter and electrodes. The redox electrode from Ingold was calibrated with Eh-buffer solution. The pH_2S measurements were carried out with an Ingold electrode (Frevort and Galster, 1978). Two sub-samples (0.5 l of the water column, 0.1 l of the fluffy layer-pore water) of the dissolved fraction $< 0.45 \mu\text{m}$ were taken. One was acidified and refrigerated and one was frozen until determination of the total and labile fraction of metals via cathodic stripping voltammetry (CSV). Additional 500-ml samples from the water column were pressure-filtered under argon through a pre-cleaned (0.1 M redist. HNO_3) nucleopore-type membrane filter (0.45 μm , polycarbonate, Schleicher and Schüll). These were kept frozen until analysis. All sampling equipment was acid-washed prior to usage.

2.2. Analysis of the particulate and dissolved metal fraction in the water column, fluffy layer and pore water

The concentrations of Zn and Cu in the particulate fraction were analyzed after total digestion of the loaded filters with graphite furnace–atomic absorption spectroscopy (GF–AAS). Mn and Fe of the particulate phase and the pore water was analyzed with inductively coupled plasma–optical emission spectroscopy (ICP–OES). The filters were dried under a clean bench in a clean room and evacuated in a desiccator until they reached constant weight. The total digestion was carried out in pressure bombs (Berghof) with 2.5 ml of concentrated redistilled HNO_3 and 200 μl hydrofluoric acid (300 μl HF for the fluffy layer). All reagents used in this study were of Merck Suprapure quality. Dilutions were prepared with Milli-

Q water. Ammonia and hydrochloric acid were purified by quartz distillation. All solutions and samples were kept refrigerated respectively frozen. The quality of the analyses was checked by the BCSS-1 (National Research Council Canada, Marine Sediment) certified reference material (CRM) by several replicate measurements. The blanks showed no signs of significant contamination. The relative standard deviations were: Mn 11%, Fe 12%, Zn 20%, and Cu 19%.

The filtrate ($< 0.45 \mu\text{m}$) fraction was analyzed for Mn, Fe, Zn, and Cu at the Oceanography Laboratories, University of Liverpool, using CSV (Autolab voltammeter (Eco Chemie) plus Metrohm hanging mercury drop electrode (663 VA stand)). Each voltammetric scan was preceded by adsorptive deposition of the metals after complexation with an added ligand on the hanging mercury drop electrode. N_2 was used to purge the cell for 5 min to remove the oxygen. Each scan was repeated three times and the measurement was repeated after addition of a standard to calibrate the sensitivity. Duplicate analyses were carried out to check the reproducibility. The relative standard deviation was generally below 20%, and for most samples $< 10\%$. The procedures applied and reagents used are listed in Table 1.

The competition between the added, known ligand, and the natural unknown ligands was used to gain information about the complex stability of the studied metals with the unknown ligand occurring naturally in the seawater. The samples for this analysis were kept frozen. All metals forming less stable complexes with ligands other than those added can be detected. With this information, a relative stability of the natural ligand was calculated by:

$$\alpha_{\text{ML}} = \frac{\alpha_{\text{MAL}}(\text{total M} - \text{labile M})}{\text{labile M}}$$

where α_{ML} is the α -coefficient for the metal/natural ligand (L) complex $\alpha_{\text{ML}} = [\text{ML}]/[\text{M}^{n+}]$; α_{MAL} is the α -coefficient for the complex with the added ligand, and labile M is the voltammetric labile fraction. Values for α_{MAL} were calculated from $\alpha_{\text{MAL}} = (\text{AL})^n \beta'_{\text{MAL}n}$, while values for $\beta'_{\text{MAL}n}$ were taken from the literature (Zn, van den Berg, 1991; Cu, Campos and van den Berg,

Table 1
Methods of metal determination via CSV^a

	Mn	Cu, Zn	
Buffer	0.01 M Tris (Tris (hydroxymethyl) aminomethane) in 0.005 M HCl	0.01 M Tris (Tris (hydroxymethyl)aminomethan) in 0.005 M HCl	<ul style="list-style-type: none"> • 0.01 M PIPES (piperazine-<i>NN</i>-bis-2-ethane sulfonic acid monosodium salt) in 0.5 M ammonia • 25 µl 0.1 M hydroxylammoniumchloride
Ligand	–	0.01 M oxine (8-hydroxyquinoline) in 0.02 HCl	20 µM 1-N-2-N in methanol
Other reagents	Ammonia to neutralize acidified samples	Ammonia to neutralize acidified samples	Ammonia to neutralize acidified sample; 1.8 mM H ₂ O ₂
Further treatment	UV-irradiation for 3 h using a 100-W mercury lamp for the determination of total metal concentration	UV-irradiation for 3 h using a 100-W mercury lamp for the determination of total metal concentration	UV-irradiation for 3 h using a 100-W mercury lamp for the determination of total metal concentration; mixture was heated in a microwave oven (60°C)
Adsorption time (s)	5–100	5–45	10–65
Equilibration time (s)	10	10	10
Deposition potential	–1.7	–1.4	–0.15
Equilibration potential	–1.3	–0.2	–0.25
Initial potential	–1.3	–0.2	–0.25
Final potential	–1.65	–1.45	–0.7
Techniques	square wave	square wave	sampled DC
Frequency	10 Hz	50 Hz	–
Modulation amplitude	0.025	0.025	–
Step potential	0.0244	0.00244	0.00366
Interval time	–	–	0.1

^a Concentrations indicated are the final concentrations in the sample.

1994; Fe, Gledhill and van den Berg, 1994) and adjusted for the salinity values recorded in this study.

To obtain the total metal concentration, the natural ligands were destroyed (UV digestion for 4 h using a 100-W medium pressure mercury lamp) prior to analysis.

2.3. Calculation of the fluxes between sediment, fluffy layer and water column

The fluxes between the fluffy layer, the sediment and the water column were calculated assuming molecular diffusion corresponding to Fick's law (Sweerts et al., 1991; Ullmann and Aller, 1982) which is valid only under steady-state conditions, and if bioturbation is neglected:

$$F = -D_S \cdot \Delta c \cdot \Delta x^{-1}$$

where F is the flux in mol cm⁻² s⁻¹, \emptyset is the dimensionless porosity, D_S is the diffusion coefficient in cm² s⁻¹, and the $\Delta c \cdot \Delta x^{-1}$ is the concentration gradient in mol cm⁻³.

The porosities of the whole cores were calculated from the weight loss after drying (0.93 for mud cores from Stations 4 and 9, and 0.73 for the till core from Station 8). The diffusion coefficients were taken from Li and Gregory (1974) and recalculated to the in situ temperature. For the calculation of the fluxes between the fluffy layer and the water column a layer of 1 mm was assumed, even though the concentration was obtained from a sample collected 40 cm above the sediment surface, since the 1-mm-thick layer above the sediment is the area where diffusion dominates. Above this layer the water column is mixed by turbulent currents.

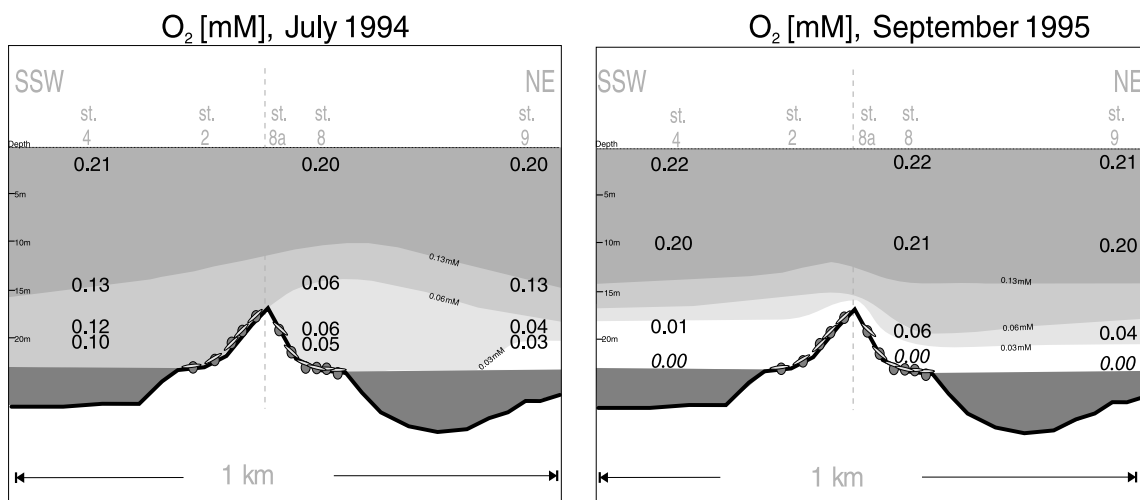


Fig. 3. Oxygen concentration (mM) at the Blinkerhügel area in July 1994 and September 1995 (italic: fluffy layer).

3. Results and discussion

3.1. Transformation of dissolved and particulate Mn-, Fe-, Zn- and Cu-species in the water column

The Mecklenburg Bight exhibits a monomictic circulation: the water column is well mixed throughout winter, spring, and autumn. The stagnant summer stratification begins usually in June and ends in September (Harms, 1996). The sampled periods cover two occasions to study the possible dependence of the formation of ferro-manganese nodules on hydrographic conditions. In general, the analyzed dissolved and particulate concentrations are in agreement with those reported by others (e.g. Kremling, 1978; Brüggmann and Matschulat, 1997).

During the July 1994 sampling campaign, the stratification was just established at a depth of 7–10 m, which led to varying intensities of oxygen

depletion over the entire study area. On the northeastern slope of the till rise Blinkerhügel, oxygen concentrations were below 0.04 mM in the bottom water (Fig. 3). Parts of the mud basins were already anoxic (Site 9). Observations of the sediment surface by divers showed that a significant amount of star fishes, mussels and other benthic organisms were using the elevated till as a refuge. During the September 1995 campaign, the stratification was found to be well established for more than 2 months and the entire bottom water was anoxic. In contrast to the situation in July 1994, no fauna could be observed and the area was nearly deserted. Video observations showed only a few, lifeless epibenthic species indicating that low oxygen concentrations in the bottom water had existed for 2–4 weeks (D. Schiedek, IOW, personal communication). Table 2 shows the geochemical parameters in the fluffy layer in September 1995. Oxygen and H₂S con-

Table 2
Geochemical parameters in the fluffy layer in September 1995

Parameter	Station 9	Station 8	Station 8a	Station 2	Station 4
<i>T</i> (°C)	15.8	15.3	14.4	14.4	14.9
pH	7.64	7.37	7.38	7.28	7.44
Alkalinity (M)	0.0017	0.0018	0.0017	0.0022	0.0018
Oxygen (mM)	n.d. ^a	0	n.d.	n.d.	0

^a Not determined.

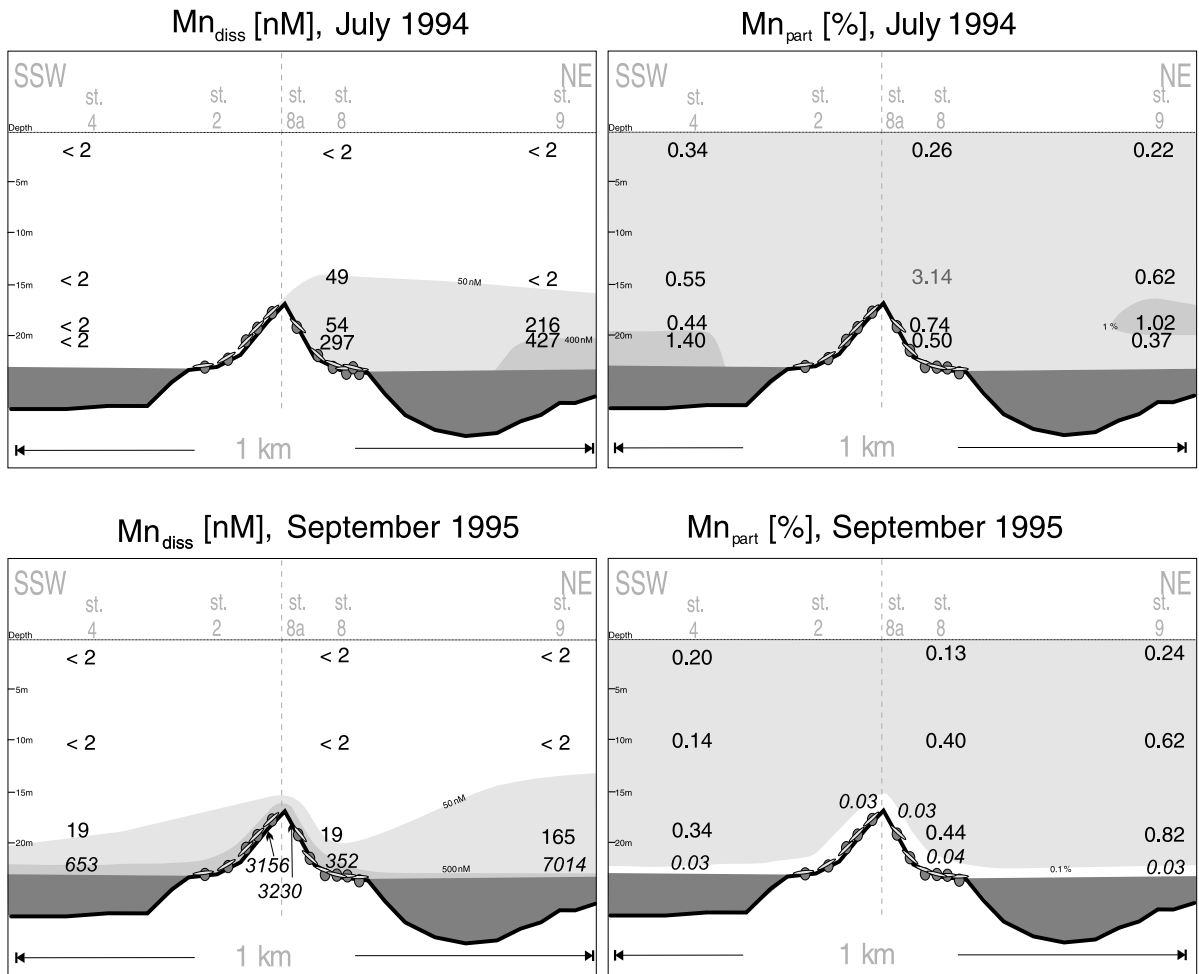


Fig. 4. Mn concentrations (nM) in the dissolved and the particulate phase (%) of the water column in the Blinkerhügel area (italic: fluffy layer).

centrations were both below the detection limit. This means that the system was sub-oxic but not yet sulfidic.

Particulate Mn (Mn_{part}) dissolves already at the beginning of the stratification period (Fig. 4). On the northeastern slope, where oxygen concentrations were below 0.04 mM, dissolved (Mn_{diss}) concentrations were up to 427 nM (Station 9) – a more than 200-fold enrichment compared to the 2 nM usually found in the oxygenated water column. Next to this station, in 18 m water depth directly above the sediment at Station 4, elevated values of Mn_{part} above 10 g kg⁻¹ occurred. This indicates that the sediment was already anoxic.

Mn^{2+} ions, remobilized from the anoxic pore waters, precipitate around suspended particles as soon as they drift into more oxygenated parts of the water column, or forming a new layer at the ferro-manganese nodules on the elevated till rise. The widespread anoxia in the Blinkerhügel area in September 1995 led to Mn_{diss} -enriched bottom water (Figs. 3 and 4). At the NE section of the Blinkerhügel area, where the anoxic conditions established earlier, the Mn_{diss} concentrations were 10 times higher than in the SSW section. The pore water of the fluffy layer even revealed Mn_{diss} values up to 7 μM (Station 9). Fe_{diss} concentrations in the bottom water in July 1994 were,

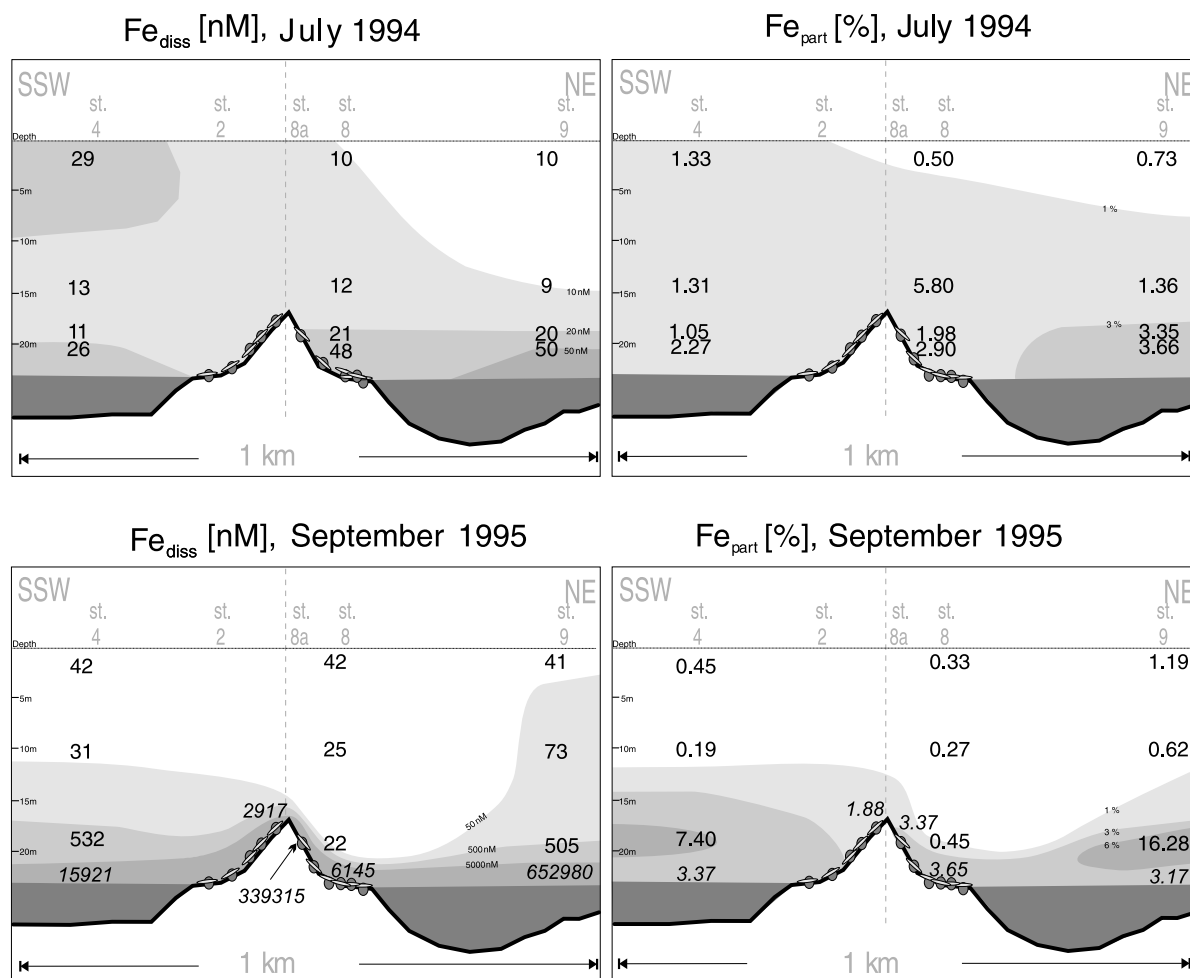


Fig. 5. Fe concentrations (nM) in the dissolved and the particulate phase (%) of the water column in the Blinkerhügel area (italic: fluffy layer).

with 50 nM, only five times higher than in the surface water, while the highest Fe_{diss} levels up to 0.65 mM were determined in September (Fig. 5).

In July 1994, the concentration of Zn_{diss} was below 50 nM, and that of Cu_{diss} was around 10 nM throughout the water column and the fluffy layer (Figs. 6 and 7). Highest concentrations for both metals (Zn 1455 nM, Cu 189 nM) were detected in the fluffy layer in September. In contrast to Mn and Fe, both elements were enriched in the fluffy layer on the less-anoxic SSW slope of the Blinkerhügel.

3.2. The fluffy layer: source for manganese, iron, zinc and copper?

The highest concentrations of Mn_{diss}, Fe_{diss}, Zn_{diss} and Cu_{diss} occurred in the fluffy layer (Figs. 4–7). Fig. 8 shows the fluxes between the fluffy layer, the sediment, and the water column, assuming molecular diffusion corresponding to Fick's law. The resulting diffusive fluxes presented in Fig. 8 must be considered as order of magnitude estimates, since steady-state conditions were assumed and bioturbation neglected. The latter, however, is justified because of the overall low

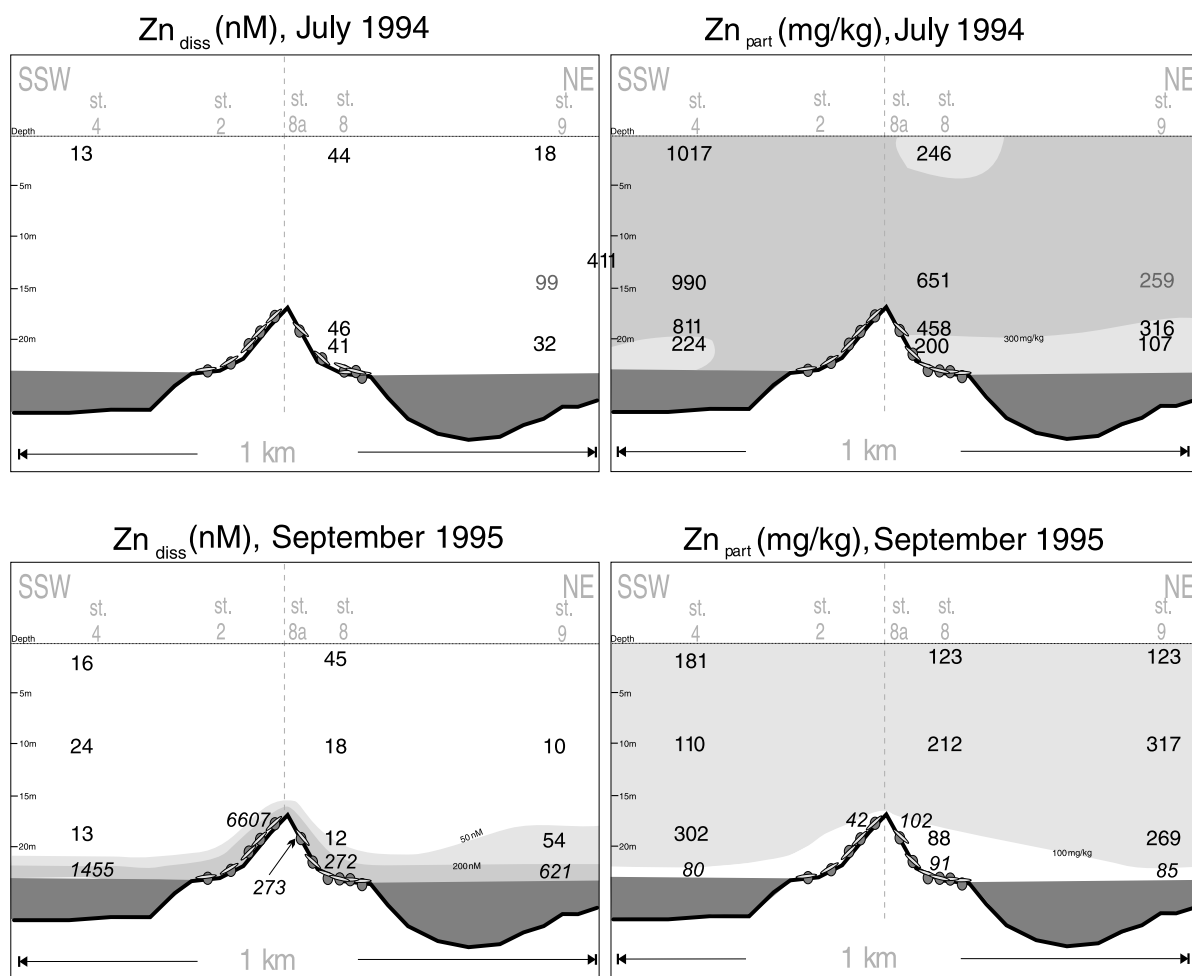


Fig. 6. Zn concentrations (nM) in the dissolved and the particulate phase (ppm) of the water column in the Blinkerhügel area (italic: fluff layer).

benthic activity at this site. Moreover the change in relative magnitude of these fluxes during the course of the year is of interest rather than absolute values. In winter, only the sediment is anoxic and a source for dissolved Mn and Fe, resulting in low Mn- and Fe-fluxes from the sediment into the water column (Harms, 1996). With the onset of stratification, the situation changes completely. The oxygen concentrations decrease in the bottom water, and the anoxic conditions rise slowly into the water column. In July 1994, the oxygen concentrations in the bottom water below 0.06 mM

were found together with enhanced Mn and Zn dissolution in the fluff layer at the sediment–water interface. This leads to elevated fluxes of both Mn_{diss} ($5.1\text{--}8.7\text{ mmol cm}^{-2}\text{ s}^{-1}$) and Zn_{diss} ($270\text{--}580\text{ }\mu\text{mol cm}^{-2}\text{ s}^{-1}$) from the fluff layer into the bottom water. The solid phase Fe is still retained (Figs. 4, 6 and 8, Table 3). In September 1995, the fluff layer experiences oxygen concentrations below 0.01 mM – conditions under which Fe starts to dissolve. Hence, significant fluxes of Fe up to $32\text{ mmol cm}^{-2}\text{ s}^{-1}$ from the fluff layer into the water column were estimated (Figs. 5 and 8).

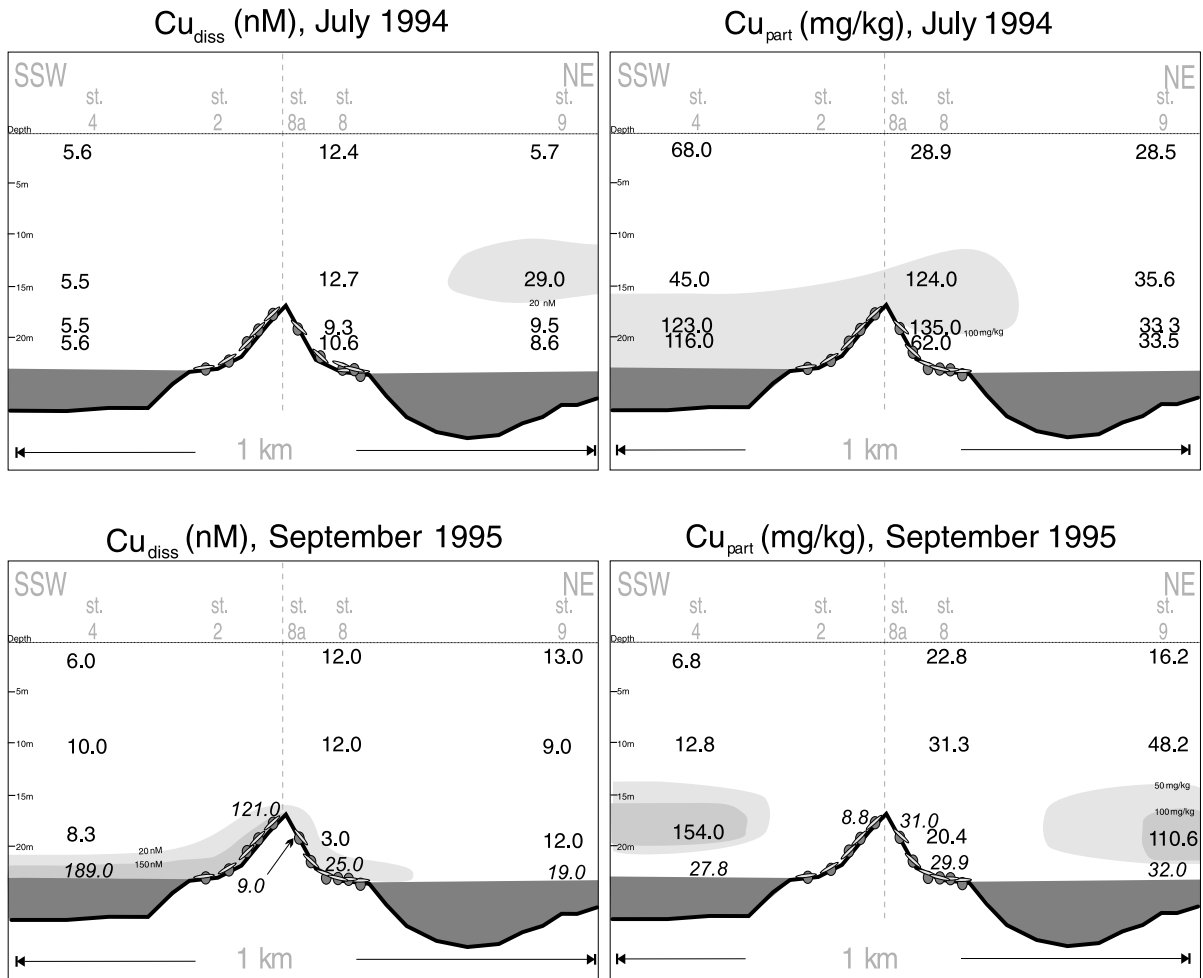


Fig. 7. Cu concentrations (nM) in the dissolved and the particulate phase (ppm) of the water column in the Blinkerhügel area (italic: fluffy layer).

3.3. Are the mobilized trace elements available for ferro-manganese nodules?

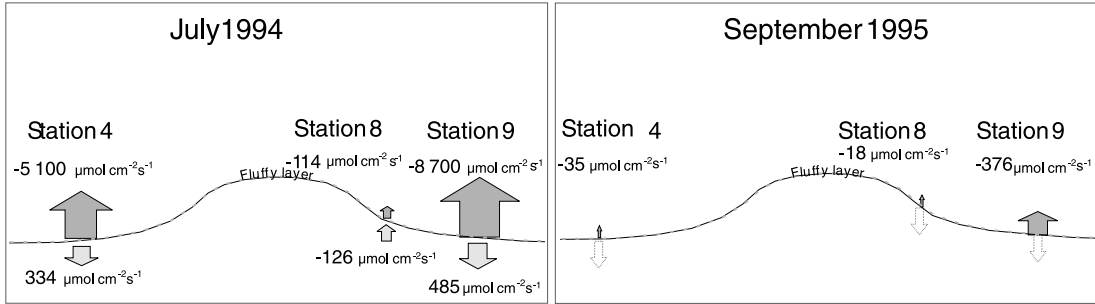
The availability of the mobilized elements for adsorption onto ferro-manganese nodules depends on the strength of competitive complexes that may be formed with ligands in the water column and in the fluffy layer. The elements are enriched in the dissolved fraction as well as in the voltammetric labile fraction (Fig. 9). However,

the log α values ($\alpha_{ML} = [ML]/[M^{n+}]$), which represent the stability of complexed Fe, Cu, and Zn in the water column and the fluffy layer, indicate that Fe and Cu are present in much stronger complexes than Zn (Fig. 10). These findings agree with studies carried out in lakes, where Zn is well known to form inorganic complexes whilst Cu and Fe rather form strong organic complexes (Sigg et al., 1995; Xue et al., 1995).

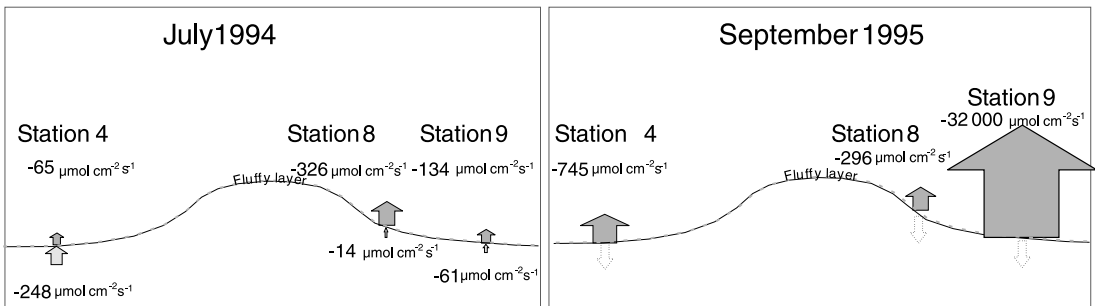
Interestingly, the complexes of Cu and Fe with

Fig. 8. Mn-, Fe-, Zn- and Cu-fluxes from the fluffy layer into the water column and into the pore water regime during stagnation periods at the Blinkerhügel (dashed arrows: after Harms, 1996).

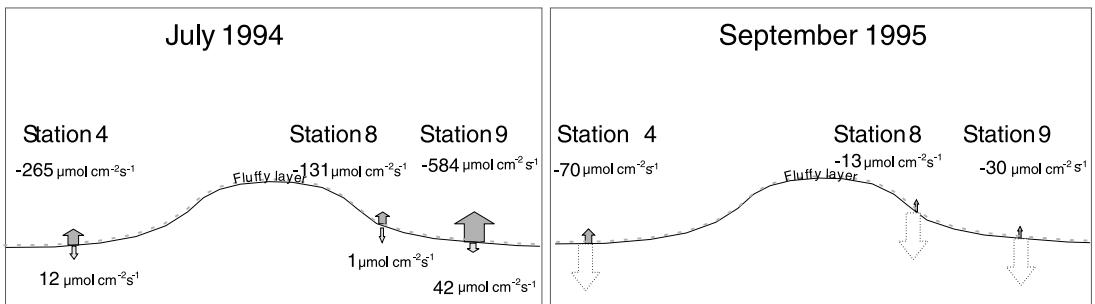
Manganese



Iron



Zinc



Copper

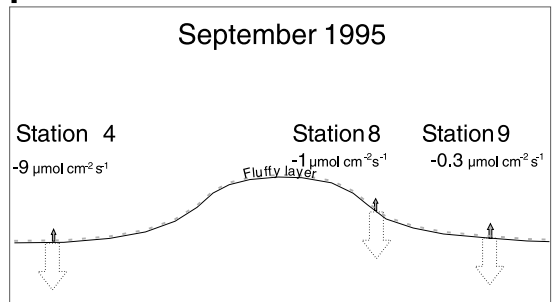


Table 3
Geochemical parameters of the pore water sampled in July 1994

Depth (cm)	Fe (μM)	Mn (μM)	Zn (μM)	pH	H ₂ S (μM)	Alkalinity (M)	SO ₄ (mM)	Chlorinity (g/l)
<i>Station 9</i>								
0–1	2.83	174.59	11.96	6.67	b.d. ^a	b.d.	b.d.	b.d.
1–2	16.29	69.79	2.72	6.42	0.4	0.030	20.7	12.9
2–3	12.59	23.28	2.69	6.25	0.1	0.002	21.7	13.9
3–4	52.61	19.06	2.77	6.10	0.1	0.003	19.5	12.6
4–5	1.13	14.91	2.66	6.22	0.4	0.003	21.3	12.4
5–6	1.36	10.68	2.68	6.46	0.4	0.004	20.7	12.5
6–7	1.86	14.76	2.58	6.54	1.1	0.005	19.4	12.4
7–8	1.47	12.98	2.63	6.61	0.4	0.006	18.1	12.3
8–9	2.44	11.38	2.51	6.66	1.6	0.007	16.4	12.1
9–10	2.85	9.74	2.43	6.77	0.9	0.007	16.9	12.1
10–12	1.43	9.99	2.42	6.76	145 844.2	0.008	16.5	12.0
12–14	1.09	9.19	2.45	6.86	171 078.0	0.010	b.d.	12.0
14–16	2.54	9.17	2.49	6.97	136 050.7	0.010	14.7	11.8
16–18	0.64	7.95	2.52	6.92	232 809.6	0.010	12.2	11.6
18–20	0.79	8.25	2.48	6.93	230 456.8	0.010	13.5	11.7
20–22	1.41	7.90	2.43	6.99	232 809.6	0.012	12.8	11.8
<i>Station 8a-21 m</i>								
0–1	66.28	0.00	0.00	7.27	b.d.	b.d.	21.0	12.8
1–2	30.92	0.35	2.84	6.97	b.d.	b.d.	18.4	12.7
2–3	b.d.	b.d.	b.d.	6.80	b.d.	b.d.	17.0	11.6
3–4	17.10	1.47	2.69	6.63	b.d.	b.d.	19.1	12.5
4–5	85.43	6.33	3.14	6.66	b.d.	b.d.	18.5	11.8
5–6	15.67	14.54	2.72	6.73	b.d.	b.d.	19.2	12.3
6–7	7.38	11.98	2.51	6.70	b.d.	b.d.	19.9	12.6
7–8	7.29	13.69	2.58	6.81	b.d.	b.d.	23.6	14.5
<i>Station 8-23 m</i>								
0–1	6.79	2.58	2.72	7.27	b.d.	b.d.	22.8	12.6
1–2	2.74	37.22	2.57	7.16	b.d.	b.d.	20.5	12.5
2–3	1.65	25.30	2.63	6.94	b.d.	b.d.	19.1	12.3
3–4	4.57	28.43	2.39	6.97	b.d.	b.d.	18.0	11.1
4–5	6.12	18.26	2.77	6.99	b.d.	b.d.	21.7	12.6
5–6	b.d.	b.d.	b.d.	7.01	b.d.	b.d.	5.1	3.1
6–7	14.88	30.09	3.04	7.00	b.d.	b.d.	18.5	12.2
<i>Station 4</i>								
0–1	1.38	102.88	5.47	6.98	b.d.	0.004	18.9	12.6
1–2	56.63	30.56	2.86	6.53	b.d.	0.003	20.1	12.6
2–3	82.86	17.09	4.62	6.34	b.d.	0.003	17.8	12.5
3–4	78.19	13.96	5.02	6.35	b.d.	0.003	18.9	12.6
4–5	72.68	13.60	2.81	6.50	b.d.	0.003	19.4	12.6
5–6	53.64	15.64	4.77	6.56	b.d.	0.004	18.0	12.6
6–7	43.12	18.33	5.34	6.74	b.d.	0.004	19.1	12.4
7–8	40.32	24.37	6.93	6.85	b.d.	0.004	18.5	12.4
8–9	30.76	30.16	2.65	6.84	b.d.	0.004	18.2	12.4
9–10	40.00	31.60	5.75	6.86	b.d.	0.005	18.6	12.2
10–12	41.49	34.40	4.22	6.95	b.d.	0.005	17.5	12.1

^a Below detection limit.

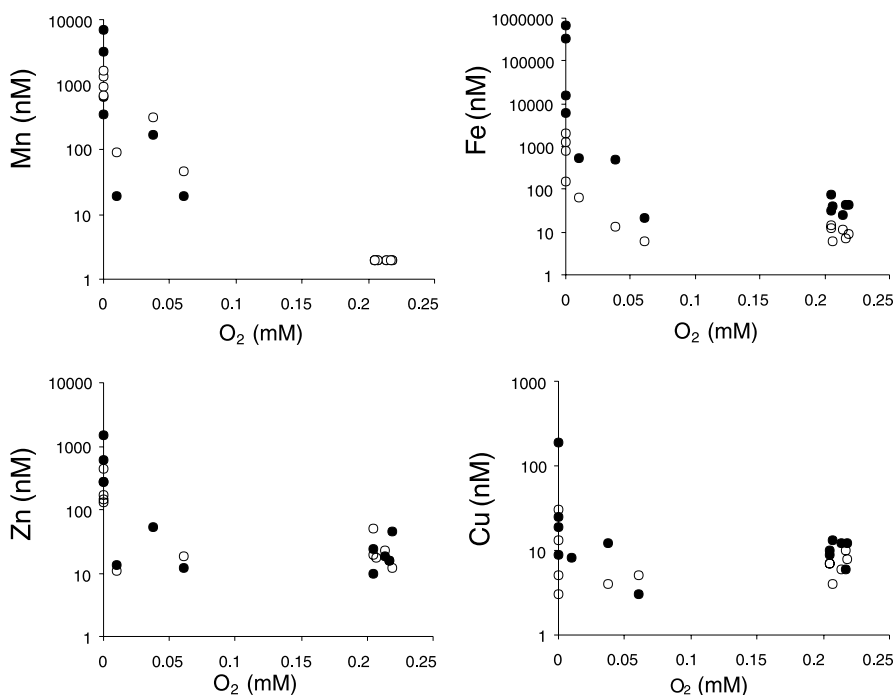


Fig. 9. The concentration of the total dissolved (filled circles) and the voltammetric labile element concentration (open circles) in the water column versus oxygen concentration shows that both fractions rise with decreasing O₂ concentration. The enhanced concentration of Mn, Fe and Zn in the voltammetric labile fraction might be available for adsorption on the Mn- and Fe-(hydr)oxides of the ferro-manganese nodules.

the natural ligands are more stable in the fluffy layer than in the water column, indicating higher ligand concentrations in the fluffy layer. This could be expected due to the proximity of large amounts of organic matter and break-down products from the fluffy layer and pore waters. The Zn/natural ligand complex has the same stability in the water column as in the fluffy layer. This means that the enhanced concentrations of Cu in the dissolved phase are less available for adsorption onto the ferro-manganese nodules. Only very small amounts of organic complexed Cu may still be adsorbed onto the nodules. This is reflected in the relatively lower Cu concentration in the ferro-manganese nodules compared to the concentration in the fluffy layer and in particles of the water column: 88% of Zn of the system ends up in the ferro-manganese nodules compared to only 45% of the Cu (Fig. 11).

4. Conclusion

The trace elements Zn and Cu remobilize in the fluffy layer. This mobilization is controlled by the oxygen distribution, which influences the dissolution of Mn- and Fe- (hydr)oxides in the fluffy layer. The reduction in O₂ in the bottom water is caused by the thermohaline stratification established regularly in summer in the western Baltic Sea. On the elevated, relatively more oxygenated till rise 'Blinkerhügel', Mn and Fe precipitate as Mn- and Fe(hydr)oxides around any available substrate and form ferro-manganese nodules. The mobilized Zn occurs in relatively weak complexes in the water column, while Cu forms stronger complexes. Zn is therefore available for sorption onto the ferro-manganese nodules to a larger extent than Cu. Accordingly, elevated Zn concentrations manifested in ferro-manganese nodules

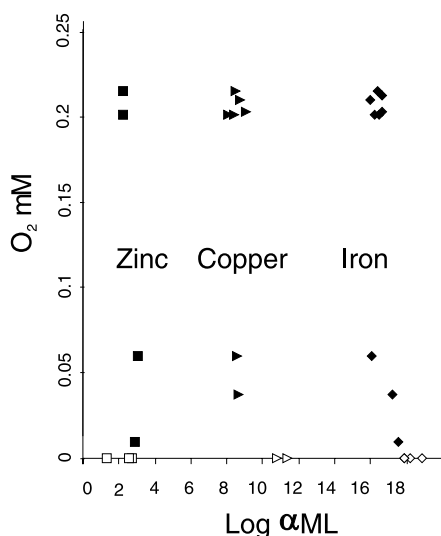


Fig. 10. Relative stability of natural complexes in the water column and the fluffy layer, expressed as $\log \alpha_{ML}$. The results of all three profiles at the Blinkerhügel site are shown (squares = zinc; triangles = copper; rhombs = iron; open symbols represent the fluffy layer).

may reflect the anthropogenic metal input into the Baltic Sea integrated over many years, while Cu is more retarded in the water column and therefore less significantly scavenged in the ferro-manganese nodules. The intense early-diagenetic regime in which the relatively fast growing ferro-manganese nodules occur clearly weakens their utility for retrospective trace element monitoring except for metals which are, like Zn, inorganically complexed.

Acknowledgements

We thank captain Albrecht and his crew of the RV *Prof. A. Penck*, the divers of the Institute for Baltic Sea Research, Warnemünde, and the team of A. Kordian for the excellent support at the sampling site. T. Leipe, A. Dahmke, F. Manheim and K. Wallmann helped with the sampling and provided useful discussions. C. Pohl helped with the analysis of the particulate fraction at her Chemistry Section laboratory of the Institute of Baltic Sea Research. D. Benesch, R. Rosenberg,

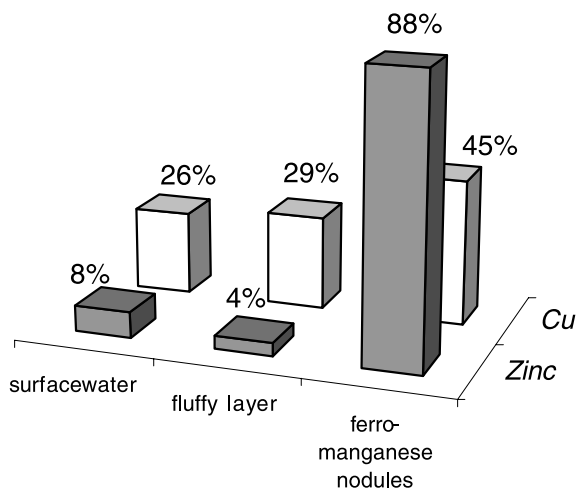


Fig. 11. Relative distribution of zinc and copper in the surface water, the fluffy layer and the ferro-manganese nodules.

J. Schulz, G. Böttcher and A. Ulrich assisted with sample preparation and analysis. R. Heath and two anonymous referees are thanked for their excellent reviews and editorial comments. The investigation was funded by the German Research Foundation (DFG HA 1834/3) and the Environmental European Research Organization (EERO).

References

- Berner, R.A., 1980. *Early Diagenesis: A Theoretical Approach*. Princeton University Press, Princeton, NJ, 256 pp.
- Berner, R.A., 1981. A new geochemical classification of sedimentary environments. *Sediment. Petrol.* 51, 359–365.
- Boström, K., Wiborg, L., Ingri, J., 1982. Geochemistry and origin of ferromanganese concretions in the Gulf of Bothnia. *Mar. Geol.* 50, 1–24.
- Brügmann, L., Matschulat, J., 1997. Zur Biogeochemie und Bilanzierung von Schwermetallen in der Ostsee. In: Matschulat, J. (Ed.), *Geochemie und Umwelt-Relevante Prozesse in Atmo-, Pedo- und Hydrosphäre*. Springer, Berlin, pp. 267–289.
- Campos, M.L.A.M., van den Berg, C.M.G., 1994. Determination of copper complexing ligand concentrations in cathodic stripping voltammetry with ligand competition by salicylaldehyde. *Anal. Chim. Acta* 284, 481–496.
- Davison, W., 1993. Iron and manganese in lakes. *Earth Sci. Rev.* 34, 119–163.
- De Vitre, R.R., Buffle, J., Perret, D., Baudat, R., 1988. A study of iron and manganese transformations at the O₂/S

- (-II) transition layer in an eutrophic lake (Lake Bret, Switzerland): a multimethod approach. *Geochim. Cosmochim. Acta* 52, 1601–1613.
- Djafari, D., 1976. Mangan–Eisen-Akkumulate in der Kieler Bucht. Ph.D. Thesis, University Kiel, Kiel.
- Frevort, T., Galster, H., 1978. Schnelle und einfache Methode zur In-situ-Bestimmung von Schwefelwasserstoff in Gewässern und Sedimenten. *Schweiz. Z. Hydrol.* 40, 199–207.
- Froelich, P.N., Klinkhammer, G.P., Bender, M.L., Luedke, N.A., Heath, G.R., Cullen, D., Dauphin, P., Hammond, D., Hartmann, B., Maynard, V., 1979. Early oxidation of organic matter in pelagic sediments of the eastern Equatorial Atlantic: suboxic diagenesis. *Geochim. Cosmochim. Acta* 43, 1075–1090.
- Ghiorse, W.C., 1980. Electron microscopic analysis of metal-depositing microorganism in surface layers of the Baltic Sea ferromanganese nodules. In: Trudinger, P.A., Walter, M.R., Ralph, B.J. (Eds.), *Biogeochemistry of Ancient and Modern Environments*. Springer, Berlin, pp. 345–354.
- Ghiorse, W.C., 1982. Isolation and properties of ferromanganese-depositing budding bacteria from Baltic Sea ferromanganese concretions. *Appl. Environ. Microbiol.* 43, 1464–1472.
- Glasby, G.P., Emelyanov, E.M., Zhamoida, V.A., Baturin, G.N., Leipe, T., Bahlo, R., Bonacker, P., 1997. Environments of formation of ferromanganese concretions in the Baltic Sea: a critical review. In: Nicholson, K., Hein, J.R., Bühn, B., Dasgupta, S. (Eds.), *Manganese Mineralization: Geochemistry and Mineralogy of Terrestrial and Marine Deposits*. *Geol. Soc. Spec. Publ.* 119, 213–237.
- Gledhill, M., van den Berg, C.M.G., 1994. Determination of Iron(III) with natural organic complexing ligands in seawater using cathodic stripping voltammetry. *Mar. Chem.* 47, 41–54.
- Grasshoff, K., Ehrhardt, M., Kremling, K., 1983. *Methods of Seawater Analysis*. Verlag Chemie, Weinheim.
- Harms, A., 1996. Untersuchungen zur Stoffdynamik in der Trübezone der Mecklenburger Bucht unter besonderer Berücksichtigung der Schwermetalle. Ph.D. Thesis, University of Rostock, Rostock.
- Heuser, H., 1988. Beobachtungen und Untersuchungen zur Genese von Flachwasser-Manganknollen in der Kieler Bucht (westliche Ostsee). *Ber. Rep. Geol. Paläontol. Inst. Univ. Kiel* 26, Kiel.
- Hlawatsch, S., 1999. Mn–Fe-Akkumulate als Indikator für Schad- und Nährstoffflüsse in der westlichen Ostsee. *Geomar Report* 85, Geomar Research Center, Kiel (with English abstract).
- Ingri, J., Pontér, C., 1987. Rare earth abundance patterns in ferromanganese concretions from the Gulf of Bothnia and the Barents Sea. *Geochim. Cosmochim. Acta* 51, 155–161.
- Kremling, K., 1978. The distribution of Mn, Fe, Zn, Cd and Cu in Baltic seawater; a study on the basis of one anchor station. *Mar. Chem.* 6, 155–170.
- Li, Y.-H., Gregory, S., 1974. Diffusion of ions in sea water and in deep-sea sediments. *Geochim. Cosmochim. Acta* 38, 703–714.
- Lovely, D.R., 1987. Organic matter mineralisation with the reduction of ferric iron: a review. *Geomicrobiol. J.* 5, 375–599.
- Mandernak, K.W., Post, J., Tebo, B.M., 1995. Manganese mineral formation by bacterial spores of the marine bacillus, strain SG-1: evidence for the direct oxidation of Mn(II) to (Mn(IV)). *Geochim. Cosmochim. Acta* 59, 4393–4408.
- Nealson, K.H., 1978. The isolation and characterization of marine bacteria that catalyze Mn oxidation. *Environ. Biogeochem. Geomicrobiol.* 3, 847–858.
- Nealson, K.H., Tebo, B.M., Rosson, R.A., 1988. Occurrence and mechanisms of microbial oxidation of manganese. *Adv. Appl. Microbiol.* 33, 279–318.
- Sigg, L., Kuhn, A., Xue, H., Kiefer, E., Kistler, D., 1995. Cycles of trace elements (copper and zinc in a eutrophic lake – role of speciation and sedimentation. In: Huang, C.P., O'Melia, C.R., Morgan, J.J. (Eds.), *Aquatic Chemistry: Interfacial and Interspecies Processes*. American Chemical Society, pp. 177–194.
- Sweerts, J.-P., Kelly, R.A., Rudd, J.W.M., Hesslein, R., Capenberg, T.E., 1991. Similarity of whole-sediment molecular diffusion coefficients in freshwater sediments of low and high porosity. *Limnol. Oceanogr.* 36, 335–342.
- Ullmann, W.J., Aller, R.C., 1982. Diffusion coefficients in nearshore marine sediments. *Limnol. Oceanogr.* 27, 552–556.
- Van den Berg, C.M.G., 1991. Monitoring of labile copper and zinc in estuarine waters using cathodic stripping chronopotentiometry. *Mar. Chem.* 34, 211–223.
- Winterhalter, B.T., Siivola, B., 1967. An electron microprobe study of the distribution of iron, manganese and phosphorus in concretions from the Gulf of Bothnia, northern Baltic Sea. *C.R. Soc. Geol. Finlande* 39, 161–172.
- Xue, H., Kistler, D., Sigg, L., 1995. Competition of copper and zinc for strong ligands in a eutrophic lake. *Limnol. Oceanogr.* 40, 1142–1152.