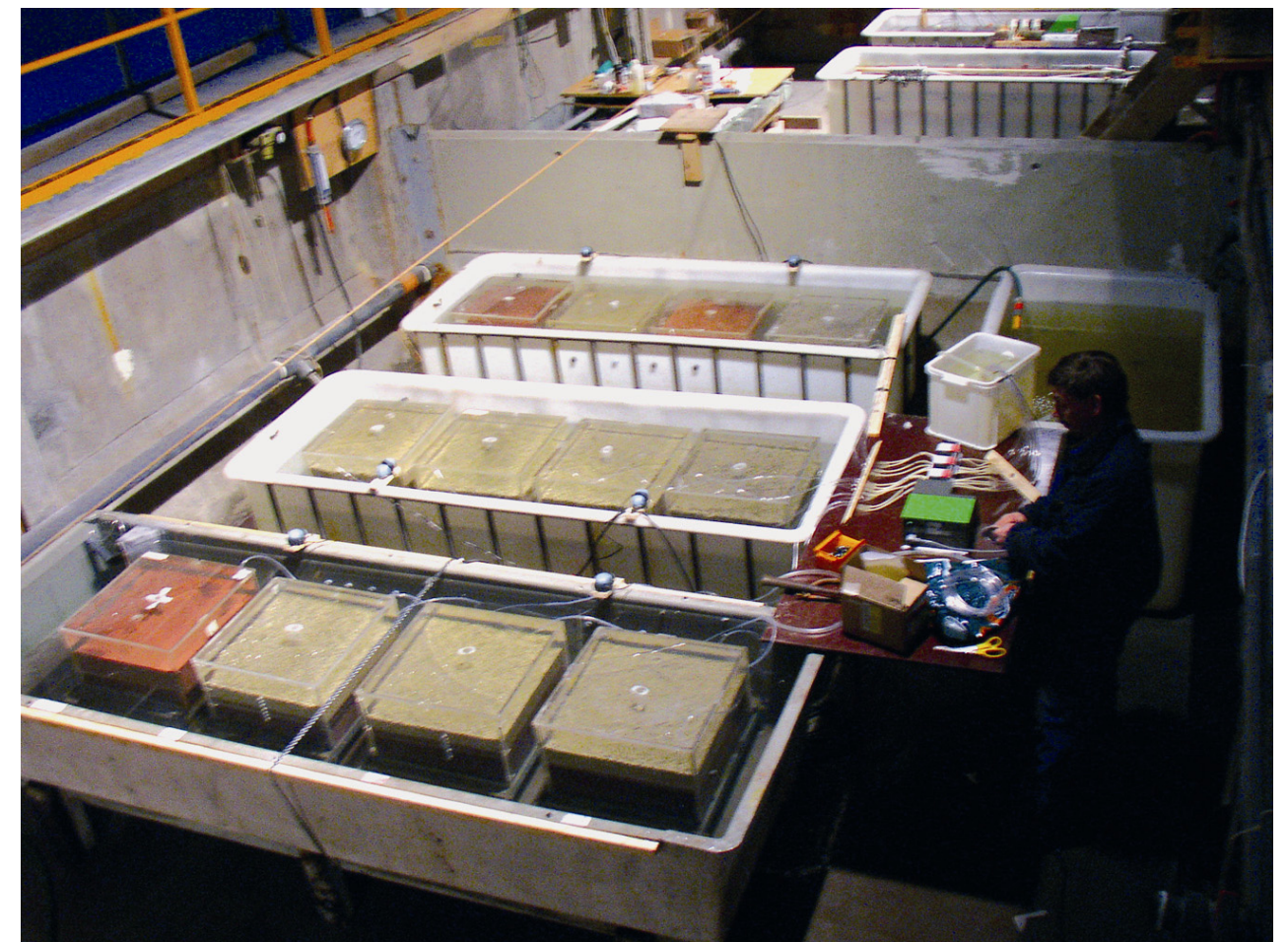




REPORT 5096-2005

Clark Island Sediment
Remediation -
Effects of a granular cap on metal fluxes



Main Office

P.O. Box 173, Kjelsås
N-0411 Oslo
Norway
Phone (47) 22 18 51 00
Telefax (47) 22 18 52 00
Internet: www.niva.no

Regional Office, Sørlandet

Televeien 3
N-4879 Grimstad
Norway
Phone (47) 37 29 50 55
Telefax (47) 37 04 45 13

Regional Office, Østlandet

Sandvikaveien 41
N-2312 Ottestad
Norway
Phone (47) 62 57 64 00
Telefax (47) 62 57 66 53

Regional Office, Vestlandet

Nordnesboder 5
N-5008 Bergen
Norway
Phone (47) 55 30 22 50
Telefax (47) 55 30 22 51

Akvaplan-NIVA A/S

N-9005 Tromsø
Norway
Phone (47) 77 68 52 80
Telefax (47) 77 68 05 09

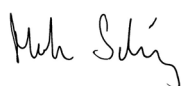
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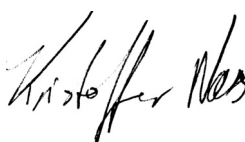
Abstract

The Clark Island remediation site is located in Francis Lake, St. Lawrence River. Capping is the selected remediation option considered for a ten ha area along the northern shores of the island where the sediments are contaminated with iron oxides and other metals. In the present project, a three-months experiment was performed on twelve mesoscale sediment-cap-water systems to assess metal fluxes within the sediments and across the sediment-water interface. Methods included *in situ* extraction of metals on passive samplers (DGT's) both in the sediment and in the water flowing across the sediment surface. Uncovered sediments were found to release Zn, Se, Mn, Cu, As, Ni, Cd and Pb, whereas no release was observed for Cr and Hg. Passive samplers (DGT-probes) revealed reduction of ferric oxides in carbon enriched sediments and substantial recycling of associated metals within the sediment-cap systems. Some evidence was found on leakage of Ni through the cap of carbon enriched sediments, but in general the cap remained highly efficient throughout the three-month period, reducing all metal fluxes (Ni included) by 89% or more. A two-layered cap was recommended using a finegrained "diffusion barrier" below a coarser top layer. The primary function of the top cap is to prevent erosion of the lower cap and to enhance downwards penetration of oxygen from the river water.

4 keywords, Norwegian	4 keywords, English
1. Tildekking	1. Capping
2. Innsjøsedimenter	2. Sediment remediation
3. Spormetaller	3. Trace metals
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Morten Thorne Schaanning
Project manager



Kristoffer Næs
Research manager
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Øyvind Sørensen
Project management director

Clark Island Sediment Remediation
Effects of a granular cap on metal fluxes

Preface

This project, NIVA O-21381 was performed for Tecsalt Inc., Montreal, Canada att. Romeo Ciubotariu in accordance with NIVA-proposal rev. 19.02.03 and contract jnr.286/03. The project is a contribution to the Clark Island Sediment Remediation Project. The experimental work was performed in the soft-bottom mesocosm at NIVA's Marine Research Station at Solbergstrand, Norway. The following persons are acknowledged for various contributions: Oddbjørn Pettersen and Sigurd Øksnevad (design, set-up, maintenance and sampling), Odvar Røyset and Eyvind Bjerke (DGT know-how, technical innovations and chemical analyses) and co-author Karl Jan Aanes (limnological know-how, collection and transfer of bioturbator organisms).

Oslo, 06.01.05

Morten Schaanning

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Executive Summary

Background

The Clark Island remediation site is located in St. Francis Lake in St. Lawrence River. In 1984, the area was declared a potential health risk for the population and a high potential risk for the environment by the Quebec Ministry of Environment. In the ongoing phase two of the project, capping is the recommended alternative for a 10 ha area along the northern shores of the island where pyrite cinders constitute a high fraction of the sediments. Pyrite cinders are an industrial waste product composed mainly of iron oxides (45-85%) contaminated with minor fractions of other metals to the extent that environmental criteria for arsenic, cadmium, copper, iron, mercury, lead, selenium and zinc are exceeded in the area.

In the present project, an experiment was performed to assess the efficiency of a granular cap to prevent release of metals to the overlying river water from Clark Island sediments contaminated with pyrite cinders. The fine-grained (92% < 63 μm) test sediment delivered from the contractor (Tecsult inc.) contained 31,5% iron (Fe) and was markedly or severely polluted with copper, arsenic, cadmium and zinc, moderately polluted with lead, but insignificantly polluted with mercury, nickel and chromium. The cap material was a 3-8 mm sand-rock fraction of dolomite/limestone delivered from a local supplier (Franzefoss Kalk AS) under the commercial name "spawning gravel". Metal analyses of the cap material yielded no concentrations exceeding the limits for insignificantly polluted.

Experimental design, methods and sample collection

The experiment was set up in twelve 50 x 50 cm boxes filled with 30 cm of solids and a 10 cm layer of overlying water. Three boxes were filled with test sediment only, another three boxes were filled with cap material only and the remaining six boxes were filled with 20 cm test sediments and a 10 cm layer of cap material. Organic matter corresponding to about 300 g C m⁻² was mixed into the test sediments in three of the six two-layered boxes before addition of the cap. Thus, the setup encountered four different treatments: T (Test sediment only), C (Cap only), TC (Capped Test sediment) and TOC (Capped Test sediment enriched with Organic carbon). Each treatment was replicated three times.

The overlying water in each box was continuously renewed from a storage tank with filtered river water sampled from a local creek. Stirring with a stream of air bubbles, ensured a well mixed and oxygenated watermass in all boxes.

After 3, 6, 9 and 12 weeks, flux of metals (F_T) were determined from water samples collected in the source water and the overlying water in each box. In addition, DGT (Diffusion Gradients in Thin-films) samplers were deployed at the same sampling locations for continuous extraction of metals during the two periods 0-6 and 6-12 weeks after set-up. At the end of the experimental period, pore water samples were drawn with a syringe through premade ports in the TC and TOC treatments. In addition, 15 cm long DGT-probes were inserted vertically from 2 cm above to 3 cm below the cap layer in three treatment boxes (C, TC and TOC). After 24 h deployment, the probes were withdrawn, rinsed and sectioned in 5 mm depth intervals to yield high-resolution vertical profiles of metal uptake.

The DGT sampler is an ion exchange resin separated from the water by a thin layer of diffusive gel and a filter. The metal fraction (C_{DGT}) sampled on a DGT is primarily free ions and weak metal complexes and hence the most bioavailable fractions of the metal. The concentrations (C_{DGT}) and the fluxes (F_{DGT}) determined from DGT-samplers, were always lower than the concentrations (C_T) and fluxes (F_T) determined from total analyses of unfiltered water samples. Thus, F_{DGT}/F_T ratios varied

from 2-3% for metals with high degree of complex formation (e.g. Pb and Cu) and up to 37-69% for metals with low degree of complex formation (e.g. Cd, Ni and Mn).

Bioturbation

Organisms (damselfly nymphs, waterlouse and chironomid larvae) were added after the first six-weeks period, but from trend analyses of the observed fluxes no evidence was found that this had any effect on the fluxes. In the uncapped sediments, this was most likely the result of low survival and reduced activity of the animals. In the capped sediments, survival was better, but because the normal depth of bioturbation of these organisms did not exceed cap thickness, increased efflux of metals was not expected and not observed.

Metal cycling within the sediment-cap system

In the pore water of the TC treatments, the concentration of all metals except Fe and Cr increased at the boundary between the cap and the test sediment. Thus iron, but not manganese, appeared to be stable in the oxidised state in the test sediment beneath the cap. Increased uptake on DGT-probes revealed fluxes of Cd, Pb, Zn and some Ni into the lower part of the cap where they appeared to reprecipitate as labile solid phases available for uptake on the probe.

In the carbon enriched (TOC) treatments, high concentrations of dissolved iron showed that ferric oxides had been reduced and simultaneous mobilisation of associated metal fractions had triggered an upwards flux of Cu and increased the upwards flux of Ni and Pb relative to those observed in TC. Deeper down in the carbon enriched test sediment, pore water concentrations of these metals as well as Zn, Cd, As and Se decreased, due to mineral formation favoured by the impact of anoxic biodegradation (e.g. sulphides, carbonates, phosphates).

In the cap layer Cd was retained below 5 cm depth, whereas Pb and Cu in the carbon enriched treatments had migrated all the way to the sediment surface at which they appeared to be captured in a thin layer of a labile, possibly organic phase revealed as narrow spikes on the DGT profiles. Zn, which is a biosessential element, showed similar spikes at the sediment water interface, in two of the three probes analysed. Even though retained in the sediment during our investigation, labile, possibly organic phases accumulating at the sediment surface must be considered to be available for uptake in organisms and spreading away from the remediation site.

Ni was not captured in the surface layer and the probe showed a steady gradient across the sediment water interface. The DGT-flux measurements from the last 6 weeks of the experiment confirmed release of Ni from the TOC-treatments. Apart from this flux of Ni, Mn was the only metal being released from capped sediments. Also this metal was released only from the TOC treatments towards the end of the experimental period. Unlike Ni, however, the flux of Mn could not be linked with the test sediment, but appeared to be mobilised by reduction and dissolution of the limited reservoir of manganese oxides present in the cap material.

Fluxes across the sediment water interface – cap efficiency

Fluxes from uncapped sediments and cap efficiencies defined as $(F_{\text{uncapped}} - F_{\text{capped}}) 100 / F_{\text{uncapped}}$ are shown in the table below. Based on the sediment concentrations, also given in the table, the test substance was classified as moderately to severely polluted with arsenic (As), cadmium (Cd), copper

	Conc. in test substance $\mu\text{g/g d.wght.}$	Release from uncapped sediment ($\text{kg km}^{-2} \text{y}^{-1}$)		Cap efficiency (% reduction)	
		Total metal (F_T)	DGT-fraction (F_{DGT})	F_T	F_{DGT}
Zinc (Zn)	1740	1730	593	101	100
Selenium (Se)	<25	160	-	100	-
Manganese (Mn)	117	149	17,4	98	89
Copper (Cu)	1160	108	18,4	103	101
Arsenic (As)	120	12	-	97	-
Nickel (Ni)	20	7,9	4,28	111	96
Cadmium (Cd)	6	2,8	1,05	102	101
Lead (Pb)	80	0,43	0,013	242	208
Mercury (Hg)	0,048	-0,00032	-	no change	-
Chromium (Cr)	18	-0,42	0,013	no change	no change
Iron (Fe)	315 000	-135	-0,58	no change	no change

(Cu), zinc (Zn) and lead (Pb) and insignificantly polluted with mercury (Hg), nickel (Ni) and chromium (Cr).

The release from uncapped sediments ranged from 1730 $\text{kg Zn km}^{-2} \text{y}^{-1}$ to 0,43 $\text{kg Pb km}^{-2} \text{y}^{-1}$. The fluxes of Hg and Cr were not significantly different from zero, and Fe was taken up from the water flowing through the boxes. The fluxes of metals available for sampling on the DGT samplers, i.e. the most bioavailable fraction, were much smaller than the total flux. The general pattern was however, similar in showing large release of Zn, a small, but significant release of Pb, no flux of Cr and uptake of Fe.

In spite of an iron concentration of 31,5%, Fe was taken up in the test sediment. Likewise, a relatively large flux of Ni was released from the test sediment in spite of a sediment concentration of 20 $\mu\text{g/g d.wght.}$, which corresponded to classification as insignificantly polluted. Thus, there was no clear relationship between metal concentrations in the sediment and the fluxes observed.

In capped sediments, fluxes were rarely significantly different from zero, yielding cap efficiencies of about 100%. Significant uptake of Ni and Pb in the capped sediments gave extraordinary high cap efficiencies of 111% for Ni_T and >200% for Pb.

Precautions

It is important to recognize that experimental work can never fully represent all aspects of the real world. In this experiment, current velocities and exchange rates of the overlying water was small compared to the conditions at the remediation site. Advective flows in the pore water resulting from possible hydrostatic pressure variations in the shoreline environment were disregarded as well as the annual variations in light and temperatures. Water quality of the experimental water was similar to that of the St. Lawrence river with regard to pH and total concentrations of e.g. Zn and Pb, but a detailed comparison e.g. with regard to organic ligands has not been done.

The most severe concern with regard to the representativity of the results of this experiment was the short time span of the experimental period and the fact that slow changes of the chemical environment in and below the cap may change cap efficiencies with time.

Internal processes observed within the cap layer by the use of DGT-probes, did indicate a potential risk of spreading of copper, lead, zinc and nickel from pyrite cinders exposed to reducing conditions

below the cap. The problem was only observed in carbon enriched test sediments and did not materialise into any severe release of metals to the watermass during this three-month experiment. It is recommended though, that actions are taken to reduce the risk of upwards migration of toxic metals from redox-boundaries in the cap layer.

Recommendations

- Metal fluxes between the contaminated sediment and the river water will be efficiently reduced by a two-layered cap with a coarser type on top of a more fine-grained quality.
- Cap thickness of 50cm of which a lower layer of about 20cm is considered appropriate for preventing leakage of metals through the cap.
- The purpose of the lower layer is to slow down upwards diffusion of metals from the contaminated sediment.
- The purpose of the top layer is to prevent erosion of the fine grained cap and to allow maximum downwards penetration of oxygen from the river water and thereby suppress upwards migration of redox boundaries within the lower layer.
- Animals are rarely found to be active at sediment depths exceeding 5cm. The two layers are therefore considered more than sufficient to prevent the cap from biological perforation.
- Good water circulation over the capped area is beneficial due to suppression of redox boundaries.
- Geotextiles may be usefull in maintaing separation between the particles in the different layers, but will presumably have little effect on metal fluxes within the cap. Geotextiles must be completely and permanently anchored throughout the capped area.

Conclusion

The experiment showed significant release of Zn, Se, Cu, As, Ni, Cd and Pb from uncapped test sediments varying between 0.43 and 1730 kg km⁻² y⁻¹. The fluxes of the most bioavailable fraction of the same metals determined on DGT-samplers were between 0,013 and 593 kg km⁻² y⁻¹. From capped test sediments, fluxes were rarely significantly different from zero, yielding cap efficiencies (flux reductions) of 96% or more. Lower cap efficiencies of 89-98% were found for Mn. Neither uncapped nor capped test sediments showed any significant release of Hg, Cr and Fe. Following the above recommendations, the granular dolomite/limestone cap appears well fit for remediation purposes.

1. Introduction

The Clark Island remediation site is situated in St. Francis Lake in St. Lawrence River upstream Quebec and Montreal. The area is contaminated with pyrite cinders, an industrial waste product composed mainly of iron oxides (45-85%) contaminated with minor fractions of other metals to the extent that environmental criteria for arsenic, cadmium, copper, iron, mercury, lead, selenium and zinc are exceeded in the area. This is in conflict with the use of the area for recreational purposes such as sight-seeing, boating, swimming, water-skiing, ice-fishing etc.. In 1984, the area was declared a potential health risk for the population and a high potential risk for the environment by the Quebec Ministry of Environment.

Contaminated sediments pose a threat to the environment due to risk of recycling of contaminants to the biosphere via resuspension, efflux or direct exposure of sediment dwelling animals and further transport via food chains. Dredging for environmental purposes alone is expensive and effectiveness may be reduced by incomplete removal and spill during dredging and transportation as well as after final treatment and/or storage (Palermo, 2003).

In situ capping is one of several alternative remediation actions. Major disadvantages may be reduced water-depth and the need for long-term monitoring and possible maintenance of the cap layer. The cap must be carefully designed to reduce contaminant efflux via diffusion or bioturbation and to withstand episodic highenergy events (storms and floods). Risk of spreading during the capping operation is, however, small compared to dredging and the cost-effectiveness may be environmental beneficial if saved resources are allocated into increased areas of remediation.

In the Clark Island remediation project, capping is the recommended alternative for a 9,66 km² area along the northern shores of the island where pyrite cinders constitute a high fraction of the sediments. The objective of this work was to perform a mesocosm simulation experiment in order to determine the efficiency of a cap in preventing efflux of metals from test sediments from Clark Island. The environment to be simulated was a shallow riverbed with slow currents and possible accumulation of organic matter. Advective flows in the pore water was assumed to be negligible, but bioturbation at the sediment-water interface may occur and increase the diffusive flux of metals through the cap. Neither toxicity nor bioaccumulation were objectives of this experiment. Accordingly, neither quantitative sampling of organisms nor analyses of metal concentration in biological samples were performed.

Ferric iron oxides is the major component of pyrite cinders in the test sediment. Anaerob decomposition of organic matter below a cap or below the sediment surface of non-capped sediment deposits, may lead to reduction and dissolution of iron oxides and trace metals adsorbed on the surface of such particles. Organic enrichment may also alter the bioavailability of trace metals through altered feeding behaviour, formation of metal-organic associations and precipitation of metal sulfides. Depending on the organic content of the test material, these processes may be more or less inherent in the set-up suggested, but in order to adress such processes separately an additional treatment was performed in which the test sediment was spiked with organic carbon.

2. Material and methods

2.1 Test substance and cap material

Six barrels of test substance were supplied from the contractor and shipped from Montreal to Oslo where they were landed 06.02.03. A few days later the barrels were transported to our laboratories at Solbergstrand Marine Research Station. Similar batches of the material were sampled from the center of each barrel and thoroughly mixed into one batch of ca 0,6 m³ using a clean concrete mixer reserved for such purposes only.

A similar amount of cap material was delivered from a local supplier (Franzefoss Kalk AS). The cap material was a 3-8 mm sand-rock fraction of Dolomite/Limestone delivered under the trade name "spawning gravel". The chemical composition (5. Appendix A.) was 84,5±5,0% CaCO₃ and 7,7±1,0% MgCO₃. Analyses of subsamples of test substance and cap material are shown in **Table 1**. Our analyses indicated a larger fine fraction (11% < 63 µm) than the one specified in Appendix A (2,5% < 200µm). However, the sample was taken from the material left-over after set-up. Due to grinding and fractionation during transport, handling and emptying of the storage container, the fine fraction given by the supplier (Appendix A) may be more representative for the cap applied in the present experiment.

Table 1. Physical and chemical characterisation of test substance and cap material. Environmental classification of test substance is shown according to Norwegian (SFT) and German (ATV) quality criteria.

Parameter	Unit	Test substance		Cap
		SFT*	ATV**	
Particle size	%<63µm	92	-	11***
TOC	mg/g d.wght.	2,1	-	9,5
Fe	"	315	-	6,7
Mn	µg/g d.wght.	117	-	252
As	"	120	II/III	IV
Cd	"	6	IV	III
Cr	"	18	I	I
Cu	"	1160	IV	IV
Hg	"	0,048	I	I
Ni	"	20	I	I
Pb	"	80	II	II
Se	"	<25	-	<25
Zn	"	1740	III	III

*Norwegian Environmental Quality Criteria for coastal sediments (Molvær *et al.*, 1997).

I=insignificantly polluted, II=moderately polluted, III=markedly polluted, IV=severely polluted. None of the metals applied to class V=extremely polluted.

**German Criteria applicable for river sediments (Ahlf *et al.*, 2002)

***Probably overestimated due to non-representative sampling (see text)

2.2 Set-up

The experiment was set up in an indoor 4,9 x 7 m concrete basin in the soft-bottom mesocosm at NIVA Marine Research Station Solbergstrand (Berge et al., 1986, Skei et al., 1996). Photos taken during set-up are shown in Figure 1. The experiment was performed in twelve 50 x 50 cm transparent, acrylic boxes filled with 30 cm of test sediments and/or cap material underneath a layer of 10 cm of continuously exchanged water (Figure 3). The four different treatments (3 replicates of each) are shown in Table 2.

Source water for the experiment (ca 3 m³) was collected from the local creek, all at once to avoid seasonal variations in water quality in the creek. The water was filtered through Micro-Wynd® filter and stored in two large plastic tanks (Figure 2) precleaned with weak acid and several batches of the creek water. Metal concentrations in the filtered creek water are shown in Table 3. A submersible pump positioned ca 10 cm above the bottom of one of the tanks circulated source water continuously into the header tank (HT) and return via overflow. From the header tank, water was further distributed to the experimental boxes using a twelve channel Watson Marlow™ peristaltic pump with marprene tubes across the rollers and transparent PVC-tubes (ID = 2 mm) on either side. The water was let into the experimental boxes horizontally 2 cm above the sediment surface and out via overflow over the rim of each box. Internal circulation in each box was driven by an air-lift system as shown in Figure 3. This also ensured well oxygenated water in all boxes.

The experimental boxes were placed in water baths (three trays, four boxes in each tray) to reduce temperature fluctuations. The water level in each tray was regulated by overflow at a constant level about two cm below the rim of the boxes.



Figure 1. Photocollage from set-up of the experiment in the Solbergstrand mesocosm.

Table 2. Test set-up.

Treatment		Test sediment	Cap material
1	Test sediment only (T)	30 cm	0 cm
2	Capped test sediment (TC)	20 cm	10 cm
4	Carbon enrichment (TOC)*	20 cm	10 cm
3	Cap only (C)	0 cm	30 cm

*Ca 300 gC m⁻² mixed into the upper 10 cm of the test sediment before addition of cap.

Table 3. Metal concentrations (µg l⁻¹) in filtered creek water sampled from header tank during the experimental period. C_T = total concentration. C_{DGT} = concentration calculated from uptake in DGT-samplers deployed in the header tank. Sampling times as shown in Table 4.

	C _T (n=4)		C _{DGT} (n=2)	C _{DGT} / C _T
	mean	± 1 std.dev.	mean	
Fe	147	± 58	0,750	1 %
Mn	5,25	± 3,77	0,110	2 %
Zn	13,8	± 5,2	4,2	30 %
Ni	1,288	± 0,085	0,250	19 %
Cd	0,0252	± 0,0076	0,0079	31 %
Cu	4,84	± 0,68	0,47	10 %
Pb	0,41	± 0,14	0,0101	2 %
Cr	0,923	± 0,723	0,020	2 %
Hg	0,012	± 0,014		
As	0,348	± 0,042		
Se	<1			

Table 4. Time schedule for sampling and other project activities. All 2003.

Date	Week	Activities
06. feb	-5	Arrival of test sediment
13. mar	0	set-up completed, initial samples of test sediment, cap, source water and "interstitial" water siphoned from the layer on top of the test sediment
17. mar	1	1 st series of DGTs deployed in overlying water
01. apr	3	water samples for Hg and ICP metals (As, Cd, Cr, Fe, Mn, Ni, Pb, Se and Zn)
25. apr	6	water samples for ICP metals DGTs collected, and 2 nd series of DGTs deployed in overlying water addition of bioturbators
14. may	9	water samples for Hg and ICP metals
27. may	11	DGT-probes for pore water deployed for 24h in three boxes (C2,TC3, TOC2)
03. jun	12	water samples for ICP metals 2 nd series of DGTs collected from overlying water pore water samples from syringe needle through ports in two boxes (TC1, TOC1) bioturbators counted

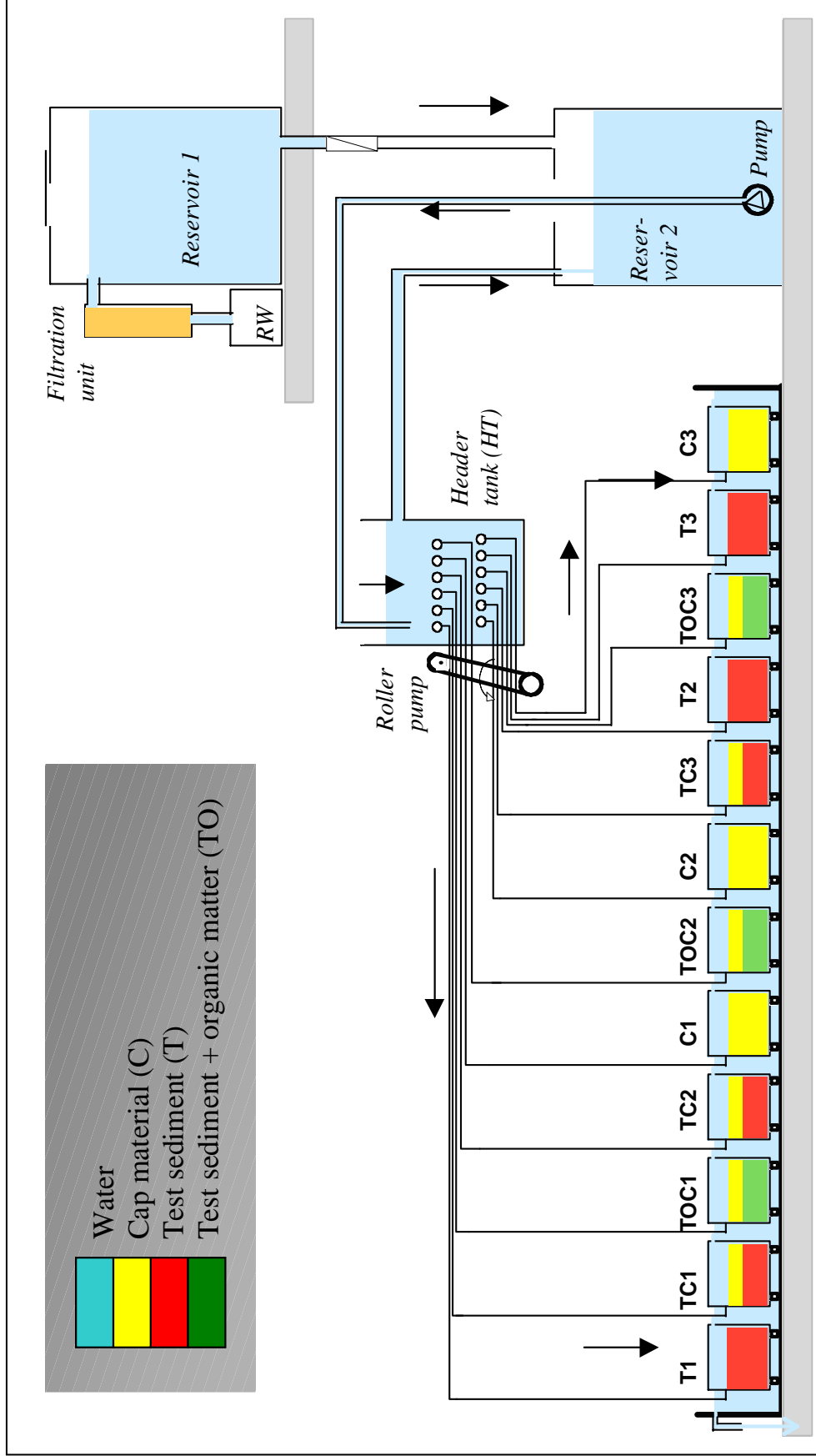


Figure 2. Set-up. Schematic drawing.

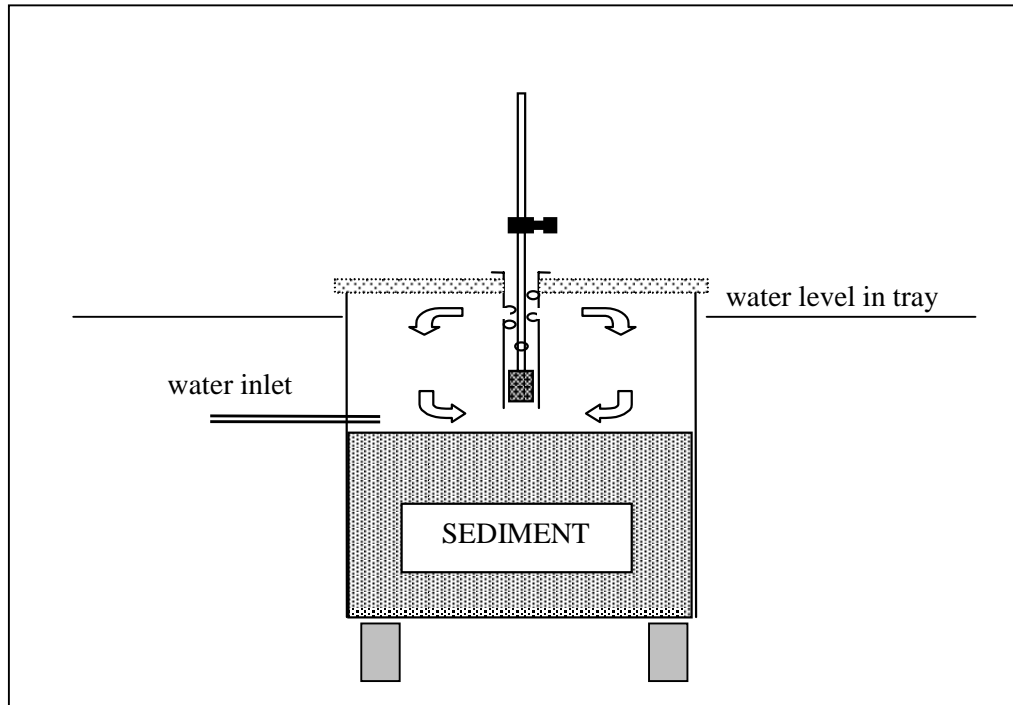


Figure 3. Schematic drawing of experimental box submerged in water bath. Water inlet from header tank and outlet over the rim of the box. The "air lift" stirring device was regularly inspected and adjusted to maintain a well mixed water layer inside each box.

Test sediment was filled into the boxes 07.03.03 and allowed to rest for 2-3 days before addition of cap material and water. The set-up was completed 13.03.03 by filling up the trays with tap water and the boxes with filtered water from the storage tanks. The boxes were filled slowly to avoid resuspension of sediment particles. The experiment was then run for a period of twelve weeks during which a comprehensive sampling programme (Table 4) was performed.

Benthic invertebrates (damselflies and waterlouses, Figure 1; low right) was collected from a mesotrophic lake and added to the test boxes 25.04.03, after the 2nd collection of water samples. In each box 5 damselfly nymphs, 35 waterlouses (*Asellus aquaticus*) and 150 midge larvae of the chironomid species *Chironomus riparius* (from our test culture) were added. After the introduction of bioturbators, small amounts of food (Tetramin) were added twice a week. For the whole experiment, less than 2 g was added to each box.

The water quality and the flow rates within each box were determined at three different occasions (Table 5). The mean temperature varied between 6,6°C and 10,0°C, and the concentration of oxygen varied correspondingly between 9,39 (77 % saturation) and 7,98 mg l⁻¹ (71 % saturation). The pH ranged 7,4-8,3 and showed no clear change with time.

Disregarding short periods of inspection and sampling, light conditions at the surface of the experimental boxes were dim ($<0.2 \mu\text{E m}^{-2} \text{s}^{-1}$).

Table 5. Water quality and flow rates in the experimental boxes.

	O ₂ (mg l ⁻¹)	Temp (°C)	pH	Flow (ml min ⁻¹)
<i>01.04.2003</i>				
min	8,61	7,00	7,80	-
max	9,20	7,80	8,30	-
mean	8,55	7,58	8,19	2,0*
stdev	0,25	0,15	0,09	-
<i>15.04.2003</i>				
min	9,00	6,6	7,50	1,84
max	9,63	6,6	7,80	1,90
mean	9,39	6,6	7,61	1,86
stdev	0,22	0,0	0,09	0,02
<i>12.05.2003</i>				
min	7,47	9,9	7,41	1,81
max	8,33	10,2	7,97	1,88
mean	7,98	10,0	7,75	1,84
stdev	0,21	0,1	0,19	0,02

*pump adjusted to yield 2,0 ml min⁻¹ by measurements in three channels only.

2.3 Sampling and analyses

All chemical analyses were performed at NIVA's laboratories in Oslo. The laboratory is accredited according to ISO 45000 standard.

2.3.1 Water and sediments

Hg was analysed using cold-vapour technique and atomic absorption. Other metals (As, Cd, Cr, Fe, Mn, Ni, Pb, Se and Zn) were determined using ICP-MS. Samples of sediments and cap material were digested in warm nitric acid before detection on ICP-AES.

2.3.2 DGT samplers

In addition to the discrete sampling of the overlying water, DGT (Diffusive Gradients in Thin-films) samplers (Davison and Zhang, 1994)(Røyset et al., 2002) were deployed in the overlying water and in the header tank for continuous sampling of metal ions. The samplers

collect metal ions on an ion exchange resin packed beneath a thin gel through which free or loosely bound metal ions can diffuse.

Standard type DGT-samplers were delivered from DGT Research Ltd., Lancaster, UK. Details can be found at www.dgtresearch.com. The samplers have been applied at NIVA since 2001 and have been found to perform well for the metals Pb, Cd, Cu, Zn, Mn, Ni, Co and Al, as well as the lanthanides (Røyset et al., 2002, 2003). Also Fe and Cr shows a significant uptake, however, the complicated aqueous chemistry of the latter two metals make uptake more dependent on environmental conditions such as change in pH, and thus more difficult to predict under variable pH-regimes.

2.3.3 Flux calculations

Assuming that the DGT samplers will not affect the concentration in the overlying water, the time-integrated flux of DGT-available metals between the sediment and the overlying water, F_{DGT} , can be calculated from the difference between the concentrations in the header tank (influx) and overlying water in each box (outflux):

$$F_{DGT} = (C_{DGT,HT} - C_{DGT,OW}) \cdot Q / A$$

in which A is the area of the sediment surface and Q is the flow of water through the respective box. Similarly, the total flux of metals, F_T , was calculated from the total concentrations determined in discrete water samples from the header tank and overlying water:

$$F_T = (C_{T,HT} - C_{T,OW}) \cdot Q / A.$$

2.3.4 Pore water

Core samples for pore water extraction from the fine-grained test material and the coarse cap material proved difficult to sample. Instead, pore water samples were drawn using a syringe with steel needle penetrating a rubber stopper in premade ports distributed at 2,5 cm (cc) intervals down the wall of two of the boxes (Figure 1, lower left). The samples were filtered through 0,45 μm acid washed membrane filters before dilution and chemical analyses using ICP-MS. Still, filtration of blanks revealed a problem with contamination of Zn of up to 80 $\mu\text{g/l}$.

In addition, pore waters were sampled using DGT probes (Davison et. al., 1997) designed for the purpose. The probes had a 150 x 17 mm “window” for diffusion of DGT-available metals from the pore water through the filter and gel onto the ion exchange resin. The probes were inserted in three different boxes leaving the upper end in the overlying water ca. 2 cm above the cap/water interface and the lower end in the test sediment ca 3 cm below the cap layer. The probes were deployed for a period of 24 hours, before retrieval and sectioning in 5 mm depth intervals before extraction of the sorbed metals and analyses using ICP-MS.

3. Results and discussion

3.1 Bioturbators

The objective of adding organisms was only to test whether their activities might have an effect on metal fluxes. Nevertheless, at the end of the test period, the uppermost 5 cm of the sediment in one randomly chosen box from each treatment was analysed for living invertebrates. As shown in **Table 6**, many of the added individuals were not found at the end of the test period. Hatching of Chironomidae was not observed during the experimental period. The reason for the low survival could be one or a combination of several factors. The set-up was not designed for testing toxicity and more than one replicate would be required for any firm conclusions. Water quality, light conditions, temperatures or some other properties of the experimental environment may have been unfavourable or different from those of their natural habitats, and the physical properties of the substrate may have been unfavourable (being either a very fine-grained test sediment or a very coarse cap).

Table 6. Retrieval of bioturbators at the end of the experiment.

Box no.	Damselflies		Waterlouses		Chironomidae	
	nos	% retrieval	nos	% retrieval	nos	% retrieval
T1	3	60	1	3	1	1
TOC1	2	40	9	26	22	15
TC2	4	80	10	29	16	11
C2	5	100	8	23	6	4

3.2 Effect of capping on pH

A small side experiment was set up to test the effects of pH of capped and non-capped sediments. Sediments, capped sediments and cap was placed in 9 beaker glasses, covered with tap water and left on the lab-bench for two months with a small stream of air (Figure 4) to maintain an oxic environment. The results are shown in Table 7.

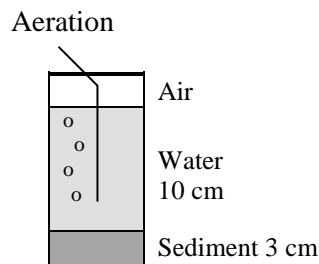


Figure 4. Small-scale set-up for test of effects on pH of the cap material.

Table 7. Measurements of pH in the water during the testperiod.

	Only Cap material			Only Test sediment			Test sediment with cap		
	A 1	A 2	A 3	B 1	B 2	B 3	C 1	C 2	C 3
27.04.03		6,72			6,72			6,72	
15.06.03	7,75	7,88	8,00	6,21	5,76	5,66	8,01	8,11	8,12
02.07.03	8,27	8,26	8,28	5,48	5,16	5,17	8,25	8,18	8,07

The results (Table 7) confirmed that the cap material acts as a buffer counteracting acidification from test sediment. This effect was not observed in the overlying water in the main set-up (Table 5), probably because the buffering processes were slow compared to the residence time of the water flowing through the boxes. In the pore water, however, the residence time is longer and an increase of pH during the experimental period is expected.

3.3 Metals in pore water

The concentration of metals in the pore water extracted 03.06. from TC1 and TOC1 is shown in Table 8 and plotted in Figure 5-Figure 7 together with the uptake on DGT-probes deployed 27.-28.05.03 in TC3 and TOC2.

3.3.1 Iron (Fe)

In TC, concentrations of Fe were low throughout the pore water sampled from the 25-175 mm depth interval (Table 8, Figure 5). The DGT uptake of up to 5000 ng was small compared to the probe uptake in TOC and confined to the test sediment below the cap. In TOC, however, the concentration of Fe had increased substantially in the test sediment layer. This increase was likely to result from reduction of ferric (FeIII) to the more soluble ferrous (FeII) iron. The upwards diffusive flux of ferrous iron (Fe^{2+} -ions) appeared to be terminated at the cap boundary at 100 mm, probably due to reoxidation to Fe(III) and precipitation as ferric oxides ($\text{Fe}(\text{OH})_3$, Fe_2O_3). However, the uptake of Fe on the DGT-probe revealed the presence of substantial amounts of labile iron up to 50 mm depth. Apparently the lower 50 mm of the cap layer is a transition zone within which Fe^{2+} is oxidised and precipitated as ferric oxides. Because the chemical environment in the transition zone is unstable with regard to iron, precipitation before filtration may easily have come about to underestimate pore water concentrations and the upwards extension of diffusion gradients into the transition zone.

The probe uptake of Fe in the transition zone was about 85 000 ng at each 5 mm depth interval. If the 17 mm wide probe extracts metals from pore water up to 20 mm away from the probe surface, and if the sediments had a wet density of $1,5 \text{ g cm}^{-3}$ and 40% water content, each probe segment can extract metals from a pore water volume of 1 ml. If so, the maximum observed concentration of $17\,000 \mu\text{g l}^{-1}$ could only account for an uptake of 17 000 ng or 20% of the observed probe uptake. According to this simplified model, more than 80% of the probe uptake must have been derived from a solid phase which dissolves rapidly by equilibration with the pore water as the probe depletes the initial pore water concentration. This solid phase is most likely a ferric oxide or oxyhydroxide recently precipitated from a saturated pore water continuously fed with a diffusive flux of ferrous iron from below. Ferric oxides

Table 8. Pore water concentrations ($\mu\text{g l}^{-1}$) in samples collected with syringe 03.06.03.

Box	Depth (mm)	Fe	Mn	Zn	Ni	Cd	Cu	Pb	Cr	As	Se
TC1	25	<100	2,9	<80	0,8	<0,05	0,9	<0,05	<1	<0,5	<10
TC1	50	<100	13	<80	1	<0,05	0,5	<0,05	1	<0,5	<10
TC1	75	<100	2,6	<80	<0,5	<0,05	0,7	<0,05	2	<0,5	<10
TC1	100	<100	31	<80	1	0,3	13	0,2	1	16	210
TC1	125	<100	166	1960	14	3,0	112	3,2	<1	19	406
TC1	150	100	680	7980	34	9,2	256	12	<1	28	210
TC1	175	<100	820	8250	44	10,8	171	3,5	<1	15	200
TOC1	25	<100	1930	<80	2,2	<0,05	1	<0,05	5,7	2	<10
TOC1	50	<100	3460	127	<0,5	<0,05	0,7	<0,05	<10	<0,5	<10
TOC1	75	<100	3480	330	<2	<0,05	0,9	<0,05	<1	<0,5	<10
TOC1	100	<100	2300	7150	16	7,6	43	2	<10	14	100
TOC1	125	11400	1740	15300	24	18	106	11,5	<10	29	71
TOC1	150	17200	785	2710	6,6	5,9	77	1,5	<10	2	20
TOC1	175	17100	577	2070	4,8	4,3	26	0,8	<10	1	10

are most probably present throughout the cap layer, but those recently precipitated in the transition zone appears to be more rapidly remobilised when the probe depletes the pore water concentration.

3.3.2 Manganese (Mn)

Like Fe, Mn is a redox sensitive metal and reduction from Mn(IV) oxides to more soluble divalent forms will increase the concentration of dissolved Mn^{2+} -ions in most natural environments. In the carbon enriched TOC, reduction of Mn(IV) is most likely involved in the formation of the Mn peak within the cap layer (50-75 mm depth). It was, however, not obvious that the source of this manganese was the test product. Probably, Mn(IV)-oxides is sufficiently abundant in the cap material to supply the observed increase in pore water concentrations during a hypothetical reduction and dissolution, from $<13 \mu\text{g l}^{-1}$ in TC to $3400 \mu\text{g l}^{-1}$ in TOC (Table 8). Also, the similarity of the pore water concentrations in the test sediment below 125 mm depth in TC ($680\text{-}820 \mu\text{g l}^{-1}$) and TOC ($577\text{-}785 \mu\text{g l}^{-1}$) gave no evidence to support mobilisation of Mn in the TOC test sediment. Furthermore, the diffusion gradients gave no evidence to support any transport of Mn by diffusion from the test sediment to the maximum at 50-75 mm depth in the cap.

Thus, in TC the pore water concentrations and DGT-uptake profiles were remarkably similar to the Fe-profiles in TOC (Figure 5), suggesting a Mn-transition zone with oxidation of upwards diffusing Mn^{2+} -ions and reversible precipitation of Mn(IV)-oxides at the cap-test sediment boundary (75-125 mm depth). It appears that oxidised iron and reduced manganese are the stable states in the test sediment. Therefore, organic enrichment does not affect manganese stability, but destabilise iron by reduction to Fe^{2+} .

In TOC then, the addition of organic carbon has triggered an upwards migration of the Mn(II)/Mn(IV) redox boundary to a depth of 50-75 mm at the time of the DGT-probe and pore water sampling. If the Mn^{2+} -ion activity is controlled by precipitation of e.g. rhodochrosite (Schaanning et al., 1988) the profile through the lower part of the cap layer might be controlled by the carbonate profile. Above the maximum (50 mm depth), the Mn(IV)-oxides of the cap material are stable, but because of the slow

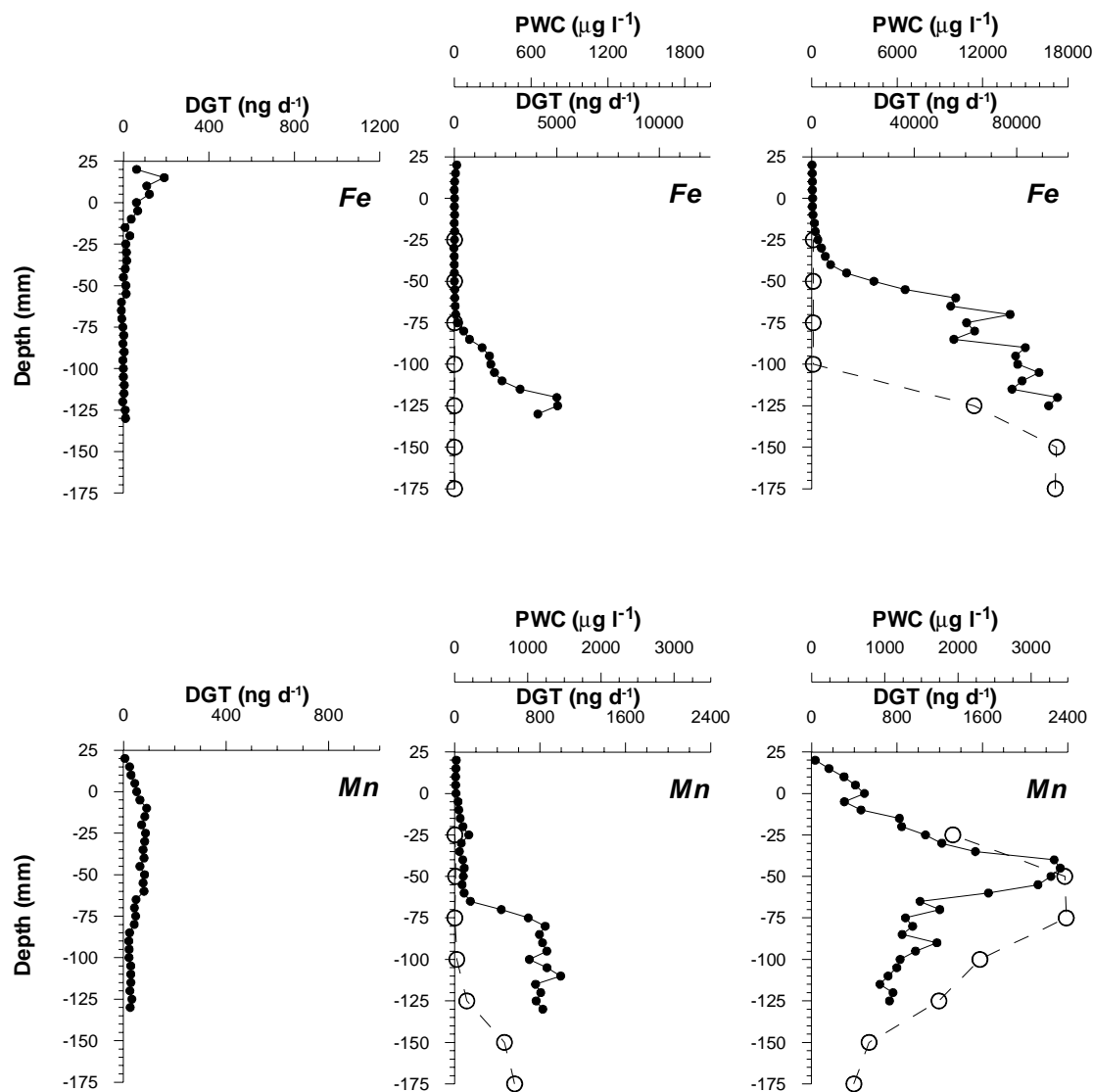


Figure 5. Pore water concentrations and DGT-probe uptake of Fe (top) and Mn (bottom) in three different treatments from left to right: C (cap only), TC (capped sediment), TOC (capped sediment with carbon added). Closed circles (lower x-axis) = DGT-probe uptake. Open circles (upper x-axis) = pore water concentration.

oxidation kinetics of the upwards diffusing Mn^{2+} -ions, the concentration of dissolved Mn has increased substantially within the upper part of the cap layer.

In the previous chapter, a DGT/PWC ratio of ca. 5:1 was found to correspond to a solid phase extraction of more than 80%, which again could explain the vertical displacement between the DGT and the PWC profiles. For Mn the DGT/PWC ratio was frequently close to 1. Using the same assumptions as above, dissolved Mn could account for most of the uptake on the DGT, which would also explain the absence of the displacement between the two Mn-profiles in TOC.

If the DGT-profile primarily reveals the distribution of dissolved Mn, the profile in TOC indicates diffusion of Mn across the cap/water interface. As shown in Figure 8, a flux of manganese was indeed observed towards the end of the experimental period. It is however, important to note that this flux

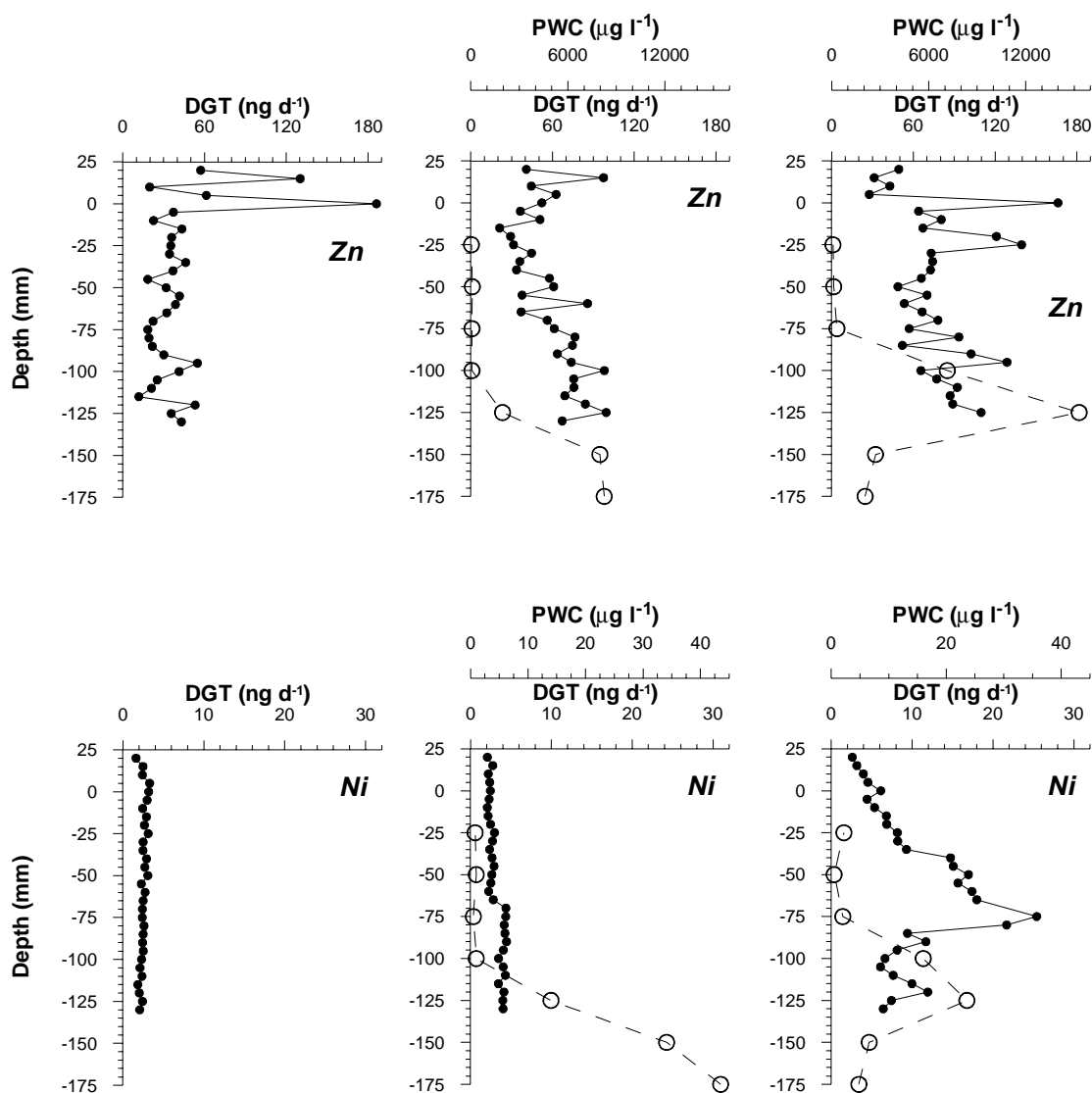


Figure 6. Pore water concentrations and DGT-probe uptake of Zn (top) and Ni (bottom) in three different treatments from left to right: C (cap only), TC (capped sediment), TOC (capped sediment with carbon added). Closed circles (lower x-axis) = DGT-probe uptake. Open circles (upper x-axis) = pore water concentration.

was the result of mobilisation from the cap material and is likely to be limited to the small reservoir of Mn-oxides present in the cap material.

3.3.3 Zinc (Zn) and nickel (Ni)

Zn and Ni was more abundant in the pore water of the test sediment in TC than in TOC (Figure 6). Precipitation of e.g. sulphides in the carbon enriched sediment is the most likely explanation of this difference. The Zn and Ni concentration maxima at 125 mm depth is a frequently observed feature at

Fe and Mn redox boundaries to the dissolution of coprecipitated or adsorbed phases. Diffusion gradients indicated a transport of dissolved Zn and Ni into the lower part of the cap where they precipitate, probably as Ni and Zn oxides (c.f. Degtiareva and Elektorowicz, 2001).

The DGT-profiles showed a slight increase of Ni in the lower part of the cap in TC. In TOC a broad maximum occurred within the Fe transition zone at 50-75 mm depth. Unlike Fe, however, the DGT/PWC ratio was low (<5) and suggested a larger fraction of dissolved Ni. Thus, the gradient on the DGT-probe indicated upwards transport by diffusion throughout the cap and across the cap/water interface. As shown in Figure 8, flux measurements by DGT-samplers tended to confirm increased release of Ni from the TOC treatment towards the end of the experiment, and unlike Mn, this flux appeared to be supported from mobilisation of Ni within the test sediment.

The DGT/PWC ratios for Zn at 100 and 125 mm depth was unreasonably low. Dissolved Zn should be taken up quantitatively by the probe, but differences between replicates or different timing of processes may explain this lack of consistency between probe uptake and pore water concentration. Within the cap layer, the ratio was about 1:1 and dissolved Zn may account for most of the probe uptake. Both pore water gradients (Table 8) and DGT-profiles indicated some upwards transport by diffusion through the cap layer in both TOC and TC (Figure 6), but in this case the gradients terminated below the cap/water interface and the flux measurements gave no evidence for release of Zn from capped sediments (Figure 11). Zn is a bioessential element and frequent maxima on the DGT-profiles at the cap/water interface (Figure 6) tended to suggest the presence of a labile solid phase, which might be bacteria or organic debris accumulated on the sediment surface. Whatever nature of this phase, in effect it appeared to prevent leakage of Zn supplied by diffusion from the test sediment.

3.3.4 Cadmium (Cd), copper (Cu) and lead (Pb)

The profiles of Cd, Cu and Pb (Figure 7) were very similar to the profiles of Zn (**Figure 6**). The pore water concentration was lowered in the carbon enriched test sediment, and maxima occurred at the depth of Fe(III) reduction and dissolution. Cu and Pb showed additional PWC-maxima at 150 mm depth in TC, which might be explained by associations with dissolved Mn(IV)-oxides below this depth.

Cd was not detectable in the pore water in the cap of either treatment, and the probe uptake was also very low above 50-75 mm depth. Thus no evidence was found for any upwards migration of Cd beyond 50mm depth in TC and 75 mm depth in TOC.

DGT/PWC ratios for the cap layers were about 5:1 for Cu and >20 for Pb. Thus, unlike Zn, the DGT-uptake of Cu and Pb within the cap appeared primarily fueled from labile solid phases. The profiles appeared to link this phase with diffusion from the test sediments. In the carbon enriched sediment (Figure 7) such gradients extended all the way to the cap/water interface, but like Zn, leakage to the water appeared to be efficiently prevented by association with some solid phase present in a narrow band close to the sediment surface. The fact that these peaks were observed in TOC only, and only at the end of more or less continuous DGT-gradients between the test sediment and the cap surface strongly suggest that the Cu and Pb phases at the sediment surface had been fed from the test sediment rather than from the water flowing through the boxes.

Even though the flux measurements confirmed no leakage from the capped sediments, the labile phases observed on the DGT-probes both on the cap surface and within the cap layer may be available to organisms settling on the cap.

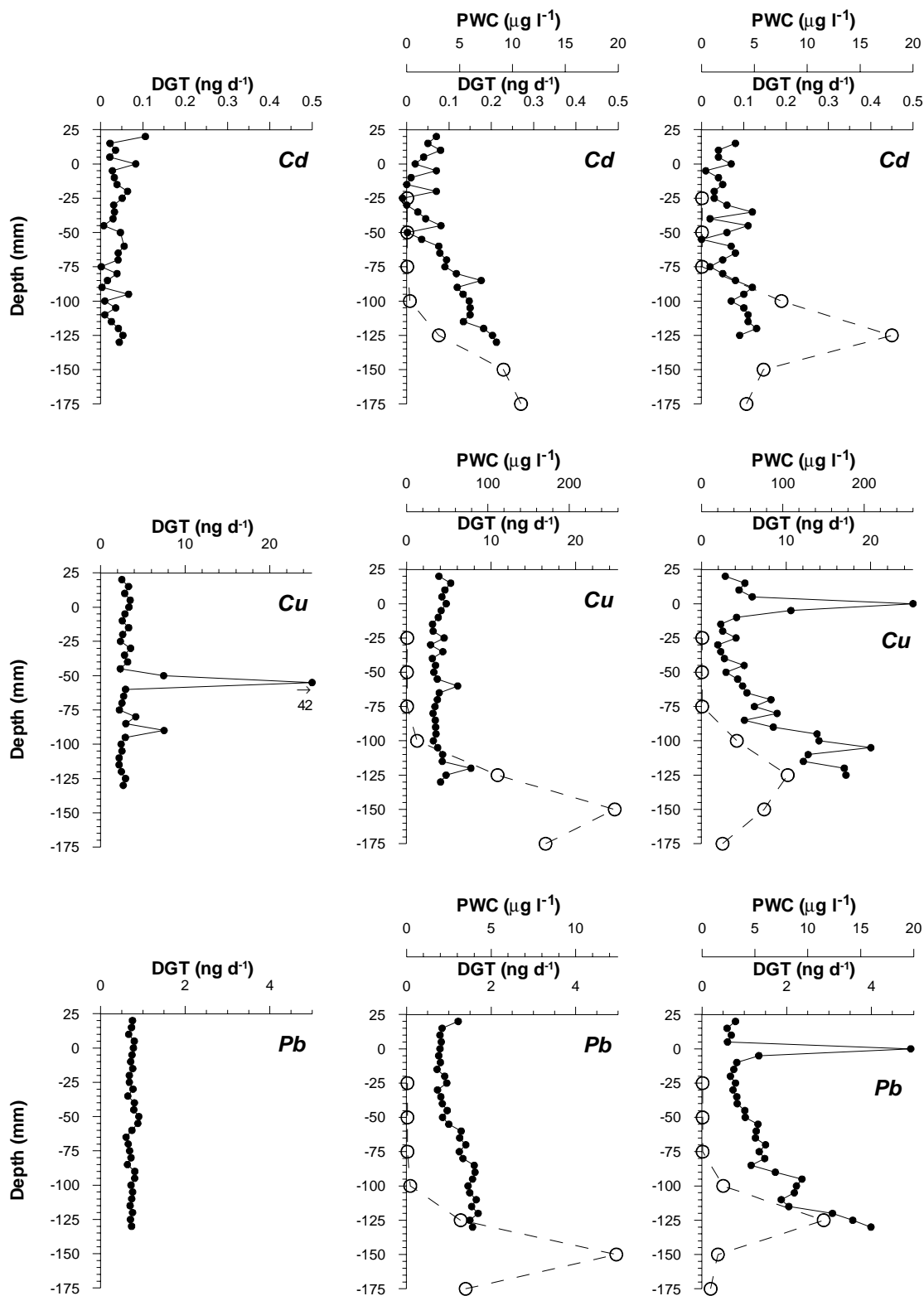


Figure 7. Pore water concentrations and DGT-probe uptake of Cd (top), Cu (middle) and Ni (bottom) in three different treatments from left to right: C (cap only), TC (capped sediment), TOC (capped sediment with carbon added). Closed circles (lower x-axis) = DGT-probe uptake. Open circles (upper x-axis) = pore water concentration.

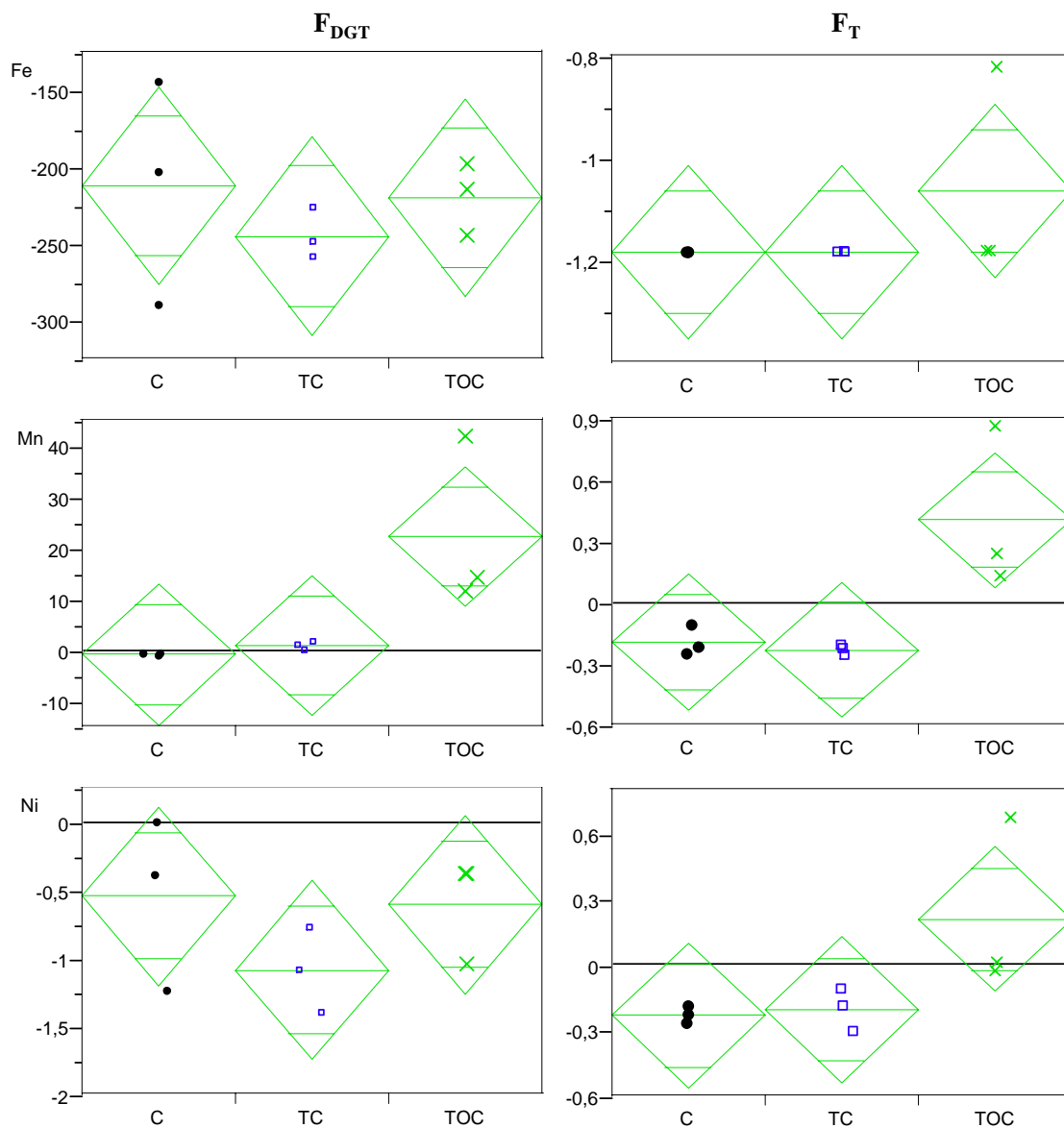


Figure 8. Comparison of fluxes of Fe, Mn and Ni determined by DGT-samplers (F_{DGT} , left-hand diagrams) and conventional water samples (F_T , right hand diagrams) in the three cap treatments C, TC and TOC. June survey only. Diamonds show mean flux and 95% confidence interval for three replicate boxes. Black line shows grand mean.

3.3.5 Arsenic (As), chromium (Cr) and selenium (Se)

These metals are not quantitatively taken up on DGT-probes, but pore water concentrations shown in Table 8, showed profiles of As and Se were quite similar to those of Cu and Pb indicating a similar behaviour to those metals. No evidence was found for upwards transport beyond 75 mm depth, but labile phases higher up in the cap layer cannot be ruled out. Flux measurements confirmed no leakage of As and Se from capped sediments (Figure 13).

Concentrations of Cr were low throughout the pore water, but interference perturbed the detection limits in particular in the TOC treatments.

3.4 Metal fluxes

Metal fluxes determined from conventional and DGT samples taken at various time intervals from the header tank and the overlying water in each box are shown in Figure 8-Figure 13. Diamond plots are used to show statistically significant differences between treatments (ANOVA, $p=0,05$). The diamonds show the mean flux for each treatment (line across center of each diamond), the 95% confidence interval (vertical span of each diamond) and the maximum allowed overlap for treatments to be significantly different at $p<0,05$ (vertical bars near top and bottom in each diamond).

Mean fluxes from capped and uncapped sediments are summarised in Table 9, and the DGT-fluxes integrated over the two periods 17.03.-25.04. and 25.04.-03.06. are compared in Table 10.

3.4.1 The DGT/total flux ratio

As a result of incomplete sampling of particulate phases and complexes, the concentrations and fluxes determined on DGTs were always smaller than the concentrations and fluxes determined from conventional samples ($C_{DGT}<C_T$, $F_{DGT}<F_T$). In particular, Cu and Pb are known to be complexed by organic matter and inorganic colloids, which probably explains why the F_{DGT} of Cu and Pb was frequently as low as 2-3% of the F_T (Table 9). Thus, F_{DGT}/F_T ratios varied from 2-3% for metals with high degree of complex formation (e.g. Pb and Cu) and up to 37-69% for metals with low degree of complex formation (e.g. Cd, Ni and Mn). The uptake of Fe and Cr on DGT-samplers are pH dependent (Røyset et al., 2002), and the low ratios ($<1,1\%$) may result from speciation and predominance of anionic complexes ($Fe(OH)_4^-/Fe(OH)_5^-$) within the prevailing pH range $6<pH<7$. The chemical speciation of Cr(III) is similar to Fe in this pH-range.

3.4.2 Cd, Cu, Zn, Pb, Mn, Ni, As and Se

These metals were released from uncapped test sediments.

Both DGT and conventional samples showed that the fluxes of Cd, Cu and Zn increased during the experimental period (Table 10), but the time series of total efflux plotted in Figure 11 and Figure 12 indicated that the efflux reached a stable level after 6-9 weeks. The efflux was significantly higher than the fluxes observed in the other treatments (C, TC and TOC) which were small and rarely significantly different from zero.

Fluxes of Pb were exceptional in the respect that this metal was significantly taken up in all cap treatments.

The efflux of Mn from the TOC treatments discussed above (ch. 3.3.2, Figure 8) was also evident from Figure 9 (F_T , time series, crosses). The plot showed that this efflux had started to develop during the sampling 14. May.

As pointed out in a previous section, both DGT-probes and samplers for flux measurements gave some evidence for release of Ni from the test sediment (ch.3.3.3, Figure 8).

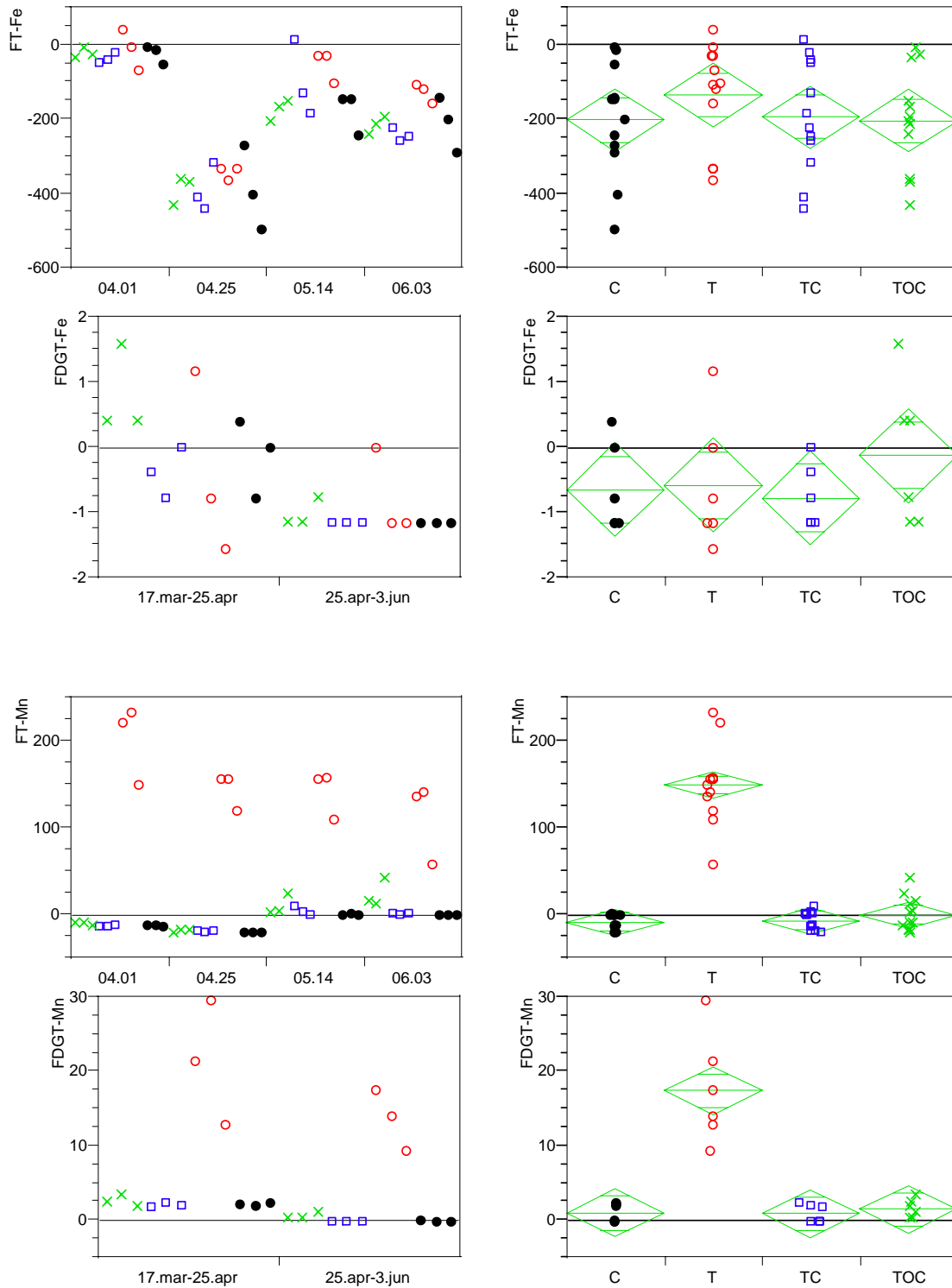


Figure 9. Total (F_T) and DGT (F_{DGT}) fluxes of Fe and Mn in treatments C (cap only), T (test sed. only), TC (test sed. and cap) and TOC (carbon enriched test sed. and cap). Variation with time is shown in left-hand diagrams. Difference between treatments is shown in right-hand diagrams. Unit = kg km⁻² y⁻¹.

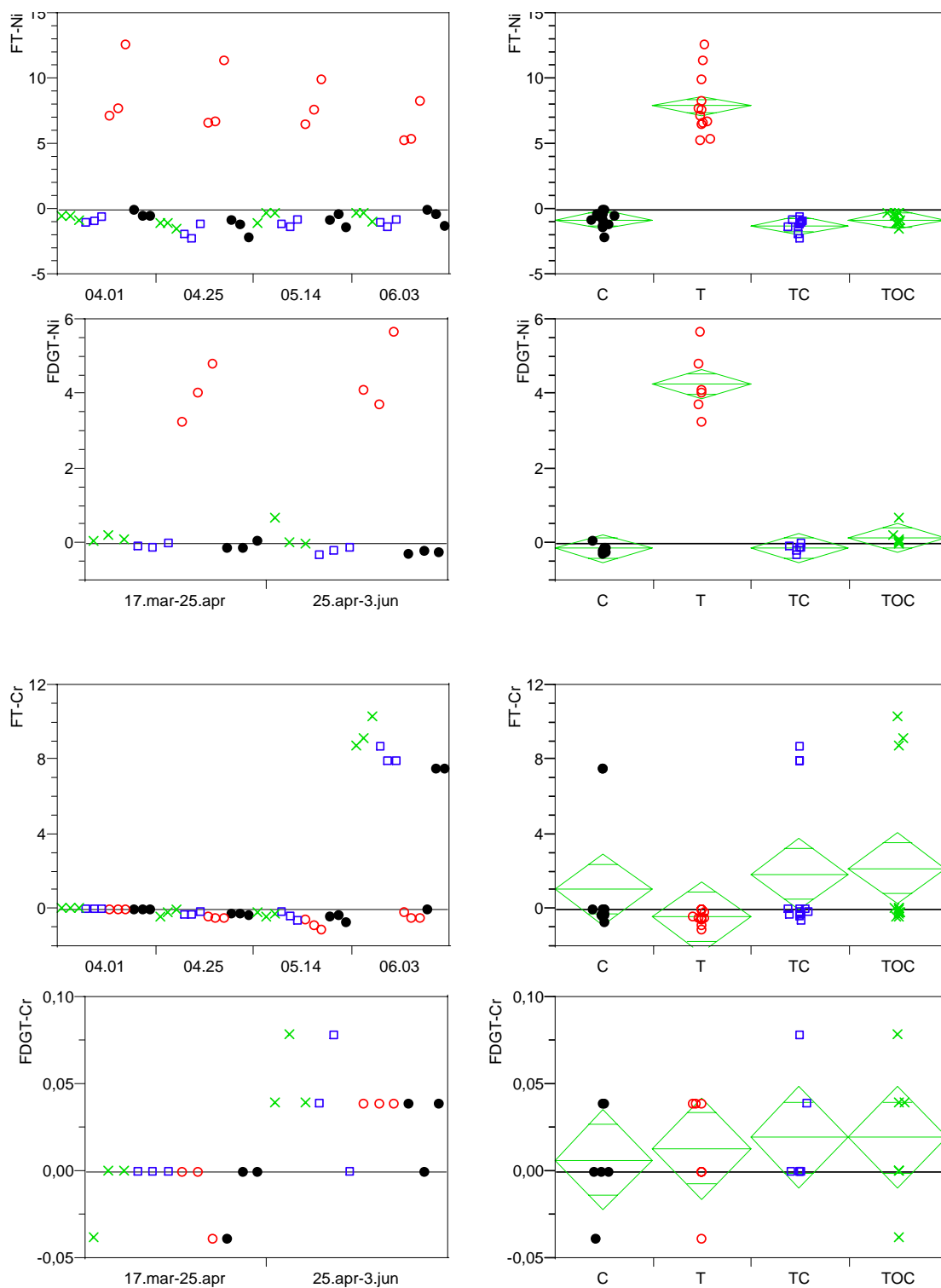


Figure 10. Total (F_T) and DGT (F_{DGT}) fluxes of Ni and Cr in treatments C (cap only), T (test sed. only), TC (test sed. and cap) and TOC (carbon enriched test sed. and cap). Variation with time is shown in left-hand diagrams. Difference between treatments is shown in right-hand diagrams. Unit = $\text{kg km}^{-2} \text{y}^{-1}$.

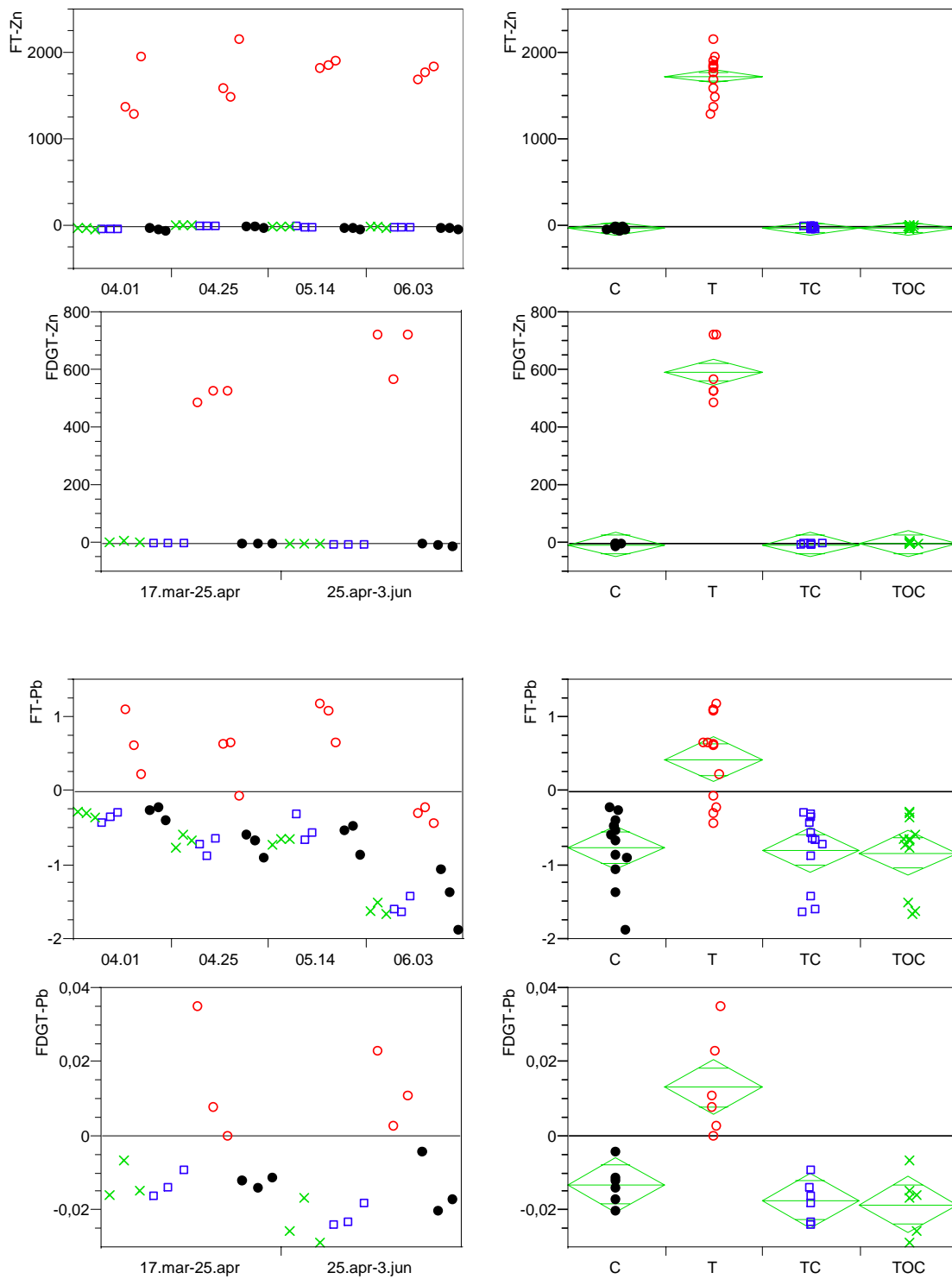


Figure 11. Total (F_T) and DGT (F_{DGT}) fluxes of Pb and Zn in treatments C (cap only), T (test sed. only), TC (test sed. and cap) and TOC (carbon enriched test sed. and cap). Variation with time is shown in left-hand diagrams. Difference between treatments is shown in right-hand diagrams. Unit = $\text{kg km}^{-2} \text{y}^{-1}$.

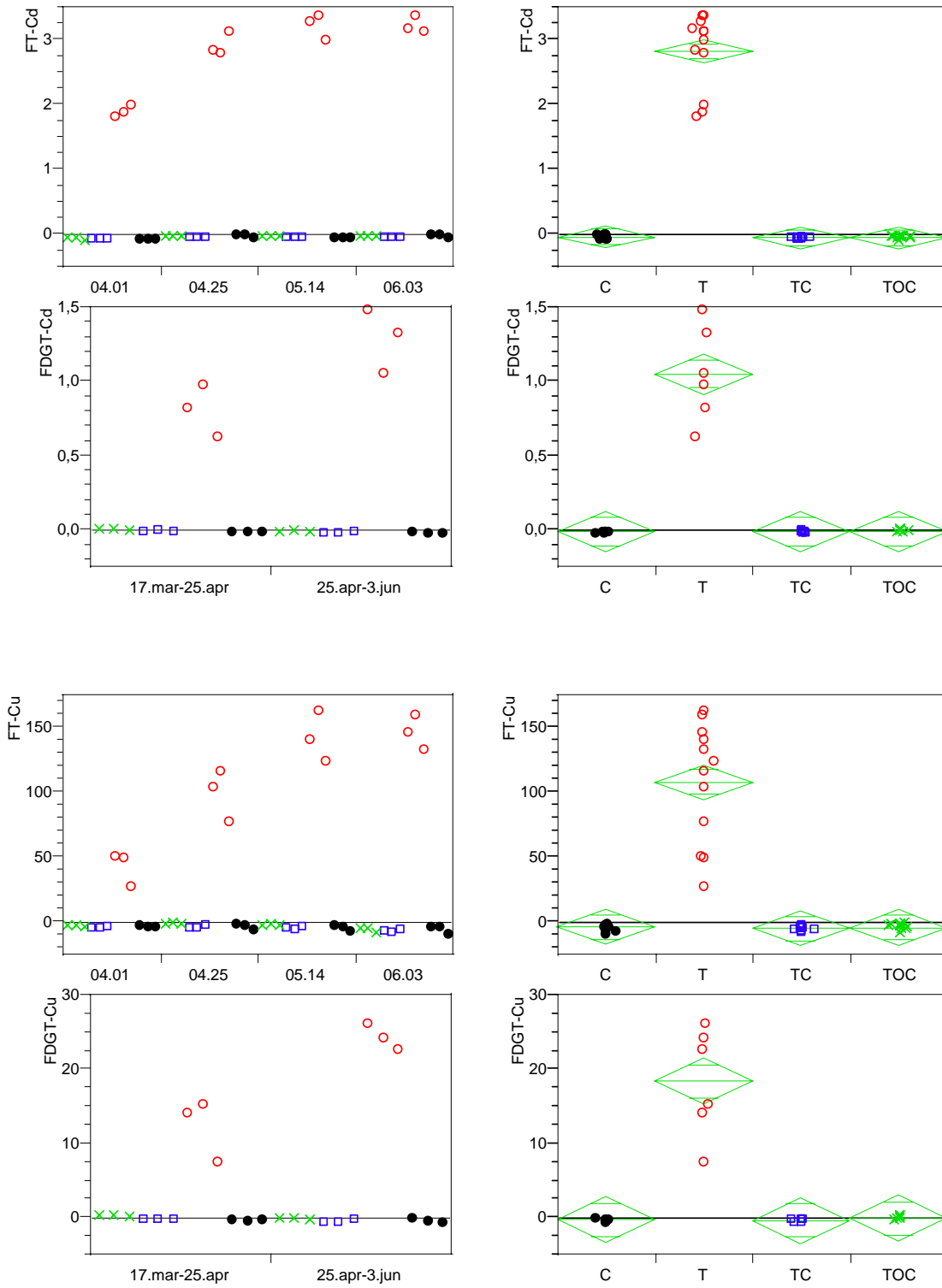


Figure 12. Total (F_T) and DGT (F_{DGT}) fluxes of Cd and Cu in treatments C (cap only), T (test sed. only), TC (test sed. and cap) and TOC (carbon enriched test sed. and cap). Variation with time is shown in left-hand diagrams. Difference between treatments is shown in right-hand diagrams. Unit = $\text{kg km}^{-2} \text{y}^{-1}$.

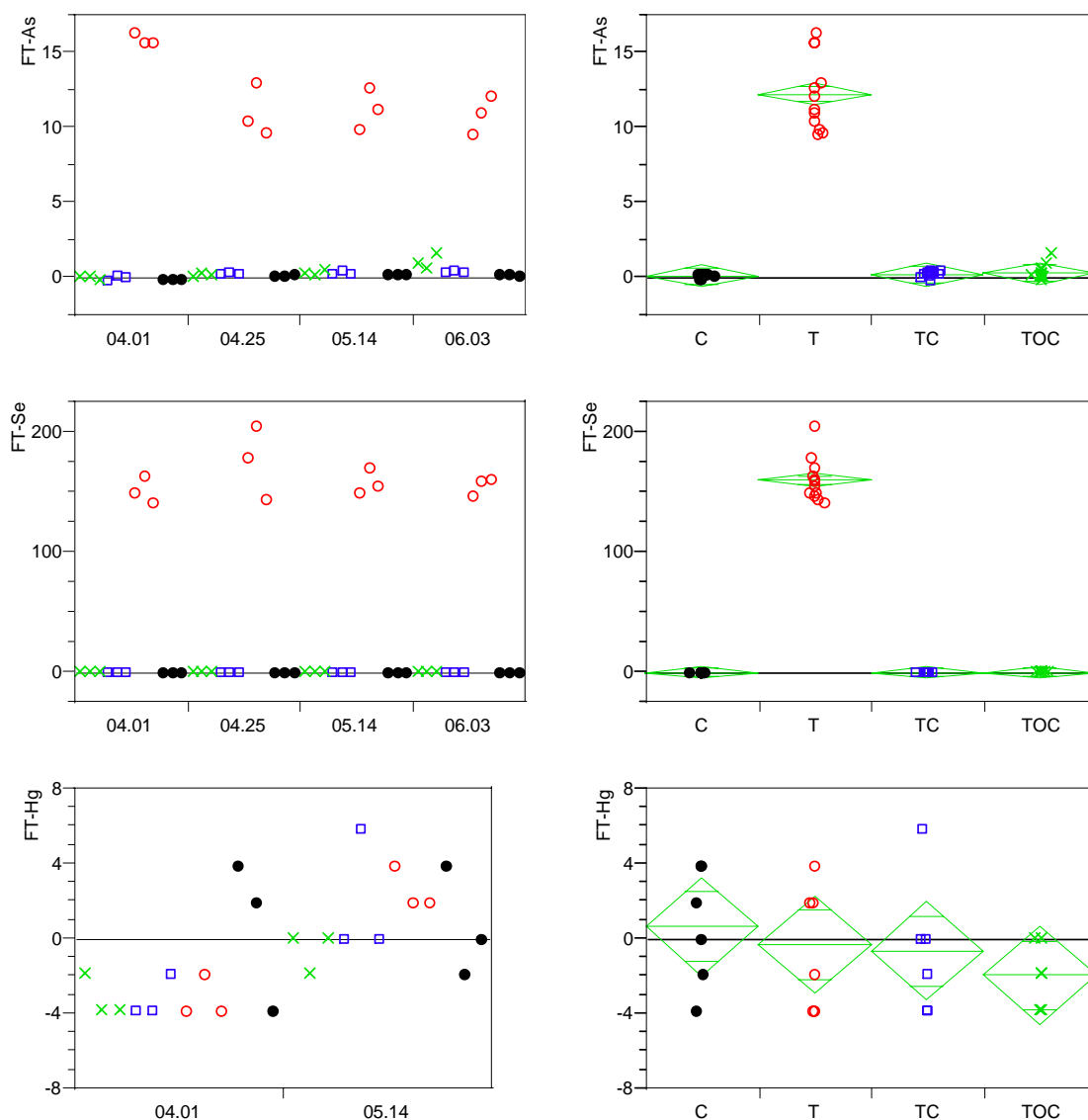


Figure 13. Total fluxes (F_T) of As, Se and Hg in treatments C (cap only), T (test sed. only), TC (test sed. and cap) and TOC (carbon enriched test sed. and cap). Variation with time is shown in left-hand diagrams. Difference between treatments is shown in right-hand diagrams. Points are scattered horizontally within each category. Units: Hg = $\text{g km}^{-2} \text{y}^{-1}$, As and Se = $\text{kg km}^{-2} \text{y}^{-1}$.

3.4.3 Fe, Cr and Hg

These metals were not released from the test sediments.

Fluxes of Fe were close to zero or negative (uptake in sediment) in most samples. No difference between treatments were observed neither for DGT nor total flux.

Fluxes of Hg were only determined at two occasions and with conventional samples only. A small uptake was observed in most of the samples taken 1. Apr. and zero flux or a small release was observed in most samples taken 14. May. In average, no difference was observed between treatments and none of the treatments yielded a mean flux significantly different from zero.

The DGT-fluxes for Cr showed zero or slightly negative fluxes during the first period and zero or slightly positive fluxes during the last period of deployment. In average, no difference was observed between treatments and none of the treatments yielded a mean flux significantly different from zero. The total flux was also close to zero in all samples collected before the last survey. In June, however, a very consistent release of 7-10 kg Cr km⁻² y⁻¹ was observed from all treatments with cap (TC, TOC and C). The concentration of Cr was low both in the cap material (13 mg kg⁻¹) and test sediment (18 mg kg⁻¹). Nevertheless, the metal reservoir in the cap material is large compared to the observed fluxes. For example, a 1 % labile fraction of the total Cr present in a 50 cm layer of the cap material has the potential to sustain a flux of 10 kg Cr km⁻² y⁻¹ for 5-10 years.

Dissolved Cr can be present either as toxic Cr(VI) compounds at highly oxidising conditions or as non-toxic Cr(III) compounds at moderately oxidising or reducing conditions (Garrels and Christ, 1965). The most common form, the non-toxic Cr(III), has many features in common with Al(III) and is known to form a variety of complexes in natural environments. In the present study, no other metal showed a behaviour similar to that of Cr, and no obvious shifts in the chemical environment was observed even though the pH in the pore water of the cap material may have increased slowly during the experimental period (Table 7). We have no evidence to conclude whether the release of Cr observed in June represented a short-term episode or the beginning of a more long-term release of Cr from the cap material, but a short-term episode due to pH-change appeared to be the most likely explanation.

3.4.4 Cap efficiencies

The effects of capping were calculated as the reduction of flux in TC and TOC treatments compared to the fluxes observed in the uncapped treatments (T). The use of the upper 95% confidence limit for the flux from capped sediments, will provide a more conservative estimate for expected flux reductions (i.e. lower cap efficiencies) than using the mean flux. Nevertheless cap efficiencies were 97% or better for the metals leaking from the test sediment. In most cases, uptake of metals in the cap provided efficiencies of more than 100%.

Table 9. Metal fluxes and effects of capping calculated as the difference between the mean flux from uncapped sediments and the upper 95% confidence limit (maximum flux) from capped test sediments in % of mean flux from uncapped sediment.

n.s. = no significant flux reduction (p > 0,05). Units: Hg = g km⁻² y⁻¹, other metals = kg km⁻² y⁻¹.

	Uncapped (T)			Capped (TC, TOC)			Effect of cap	
	F _T	F _{DGT}	F _{DGT} /F _T	Upper 95% confidence limit			Calc. flux reduction	
	F _T	F _{DGT}	F _{DGT} /F _T	F _T	F _{DGT}	F _{DGT} /F _T	F _T	F _{DGT}
Cd	2,82	1,05	37%	-0,044	-0,0075	17%	102%	101%
Cu	107,9	18,4	17%	-3,6	-0,081	2,2%	103%	101%
Ni	7,93	4,28	54%	-0,83	0,164	-	111%	96%
Pb	0,43	0,013	3%	-0,61	-0,014	2,3%	242%	208%
Zn	1730	593	34%	-22,3	-2,011	9%	101%	100%
As	12,25	-	-	0,425	-	-	97%	-
Se	160	-	-	0	-	-	100%	-
Mn	149	17,4	12%	2,78	1,915	69%	98%	89%
Fe	-135	-0,58	0,4%	-140	0,102	-	n.s.	n.s.
Hg	-0,32	-	-	0,48	-	-	n.s.	-
Cr	-0,42	0,013	-	3,7	0,042	1,1%	n.s.	n.s.

3.4.5 Flux trends

Change with time of the fluxes may result from increased exchange between pore water and overlying water after addition of bioturbators or altered rates of physical and chemical processes as the sediment-water system moves from initial instability towards a more steady state. Absolute fluxes must be considered because increased bioturbation should, if significant, make negative fluxes more negative and positive fluxes more positive. However, a shift of flux direction would not be expected to result from increased bioturbation.

A consistent increase of the DGT-fluxes was only observed for Zn, Cu and Cd (Table 10). Significant decrease of Mn in the capped sediments and significant flux changes involving changed flux direction for Cr in both treatments and Fe in capped sediments require some other explanation than increased bioturbation.

For the total fluxes (F_T) trends were analysed using linear regression. Two examples yielding good correlation coefficients ($r^2 > 0,6$) and significant trends ($p < 0,05$) in opposite directions (slopes: $\alpha_{As} = 0,016$, $\alpha_{Pb} = -0,018$) are shown in Figure 14. Slopes and p-values for all regressions yielding $p < 0,05$ are listed in Table 11.

Table 10. Trends of absolute DGT fluxes from capped (C, TC, TOC) and uncapped (T) sediments during the two time intervals. n.c. = no significant change (ANOVA, t-test, $p = 0,05$). dir. c. = direction change. Units = $\text{kg km}^{-2} \text{y}^{-1}$.

	Capped (C, TC, TOC)				Uncapped (T)			
	17.03.- 03.06.	17.03.- 25.04	25.04.- 03.06.	p	17.03.- 03.06.	17.03.- 25.04	25.04.- 03.06.	p
Zn	increase	-1,30	-8,30	<0,0001	increase	515	672	0,04
Cu	increase	-0,155	-0,367	0,038	increase	12,3	24,4	0,01
Cd	increase	-0,007	-0,018	<0,0001	increase	0,81	1,29	0,04
Ni	n.c.	-0,004	-0,078	>0,05	n.c.	4,1	4,5	>0,05
Pb	increase	-0,013	-0,020	0,016	n.c.	0,014	0,012	>0,05
Mn	decrease	2,165	-0,009	<0,0001	n.c.	21,2	13,6	>0,05
Cr	dir.c.	-0,009	0,039	0,0004	dir.c.	-0,013	0,039	0,02
Fe	dir.c.	0,086	-1,124	0,0001	n.c.	-0,389	-0,778	>0,05

Table 11. Trends of total metal flux ($F_T = F_{T0} + \alpha d$) in the various treatments. Slopes (α) and p-values calculated by linear regression analyses (n=12). Unit $F_{T0} = \text{kg km}^{-2} \text{y}^{-1}$ ($\text{g km}^{-2} \text{y}^{-1}$ for Hg).

	C			TC			TOC			T		
	F_{T0}	α	p	F_{T0}	α	p	F_{T0}	α	p	F_{T0}	α	p
As	-,10	,0043	,002	-0,08	,006	,003	-0,5	,016	,002	16	-,074	,007
Cd	-,07	,0007	,03	-0,07	,0005	,0003	-0,09	,0007	,002	1,7	,021	,0002
Cr	-2,5	-	>,05	-4,0	,11	,007	-4,6	,131	,007	-0,02	-	>,05
Cu	-1,8	-	>,05	-2,9	-	>,05	-1,6	-	>,05	20	1,71	,0001
Zn	-35	-	>,05	-39	-	>,05	-34	-	>,05	1525	-	>,05
Hg	,65	-	>,05	-5,5	-	>,05	-4,4	-	>,05	-5,8	,136	,003
Pb	,06	-,02	,002	,03	-0,02	,002	0,11	-0,02	,0001	1,0	-	>,01
Ni	-,70	-	>,05	-1,2	-	>,05	-1,1	-	>,05	10	-	>,05
Se	0	-	>,05	0	-	>,05	0	-	>,05	160	-	>,05
Mn	-22	,262	,011	-24	,32	,007	-32	,62	,004	217	-1,31	,01
Fe	-193	-	>,05	-205	-	>,05	-194	-	>,05	-163	-	>,05

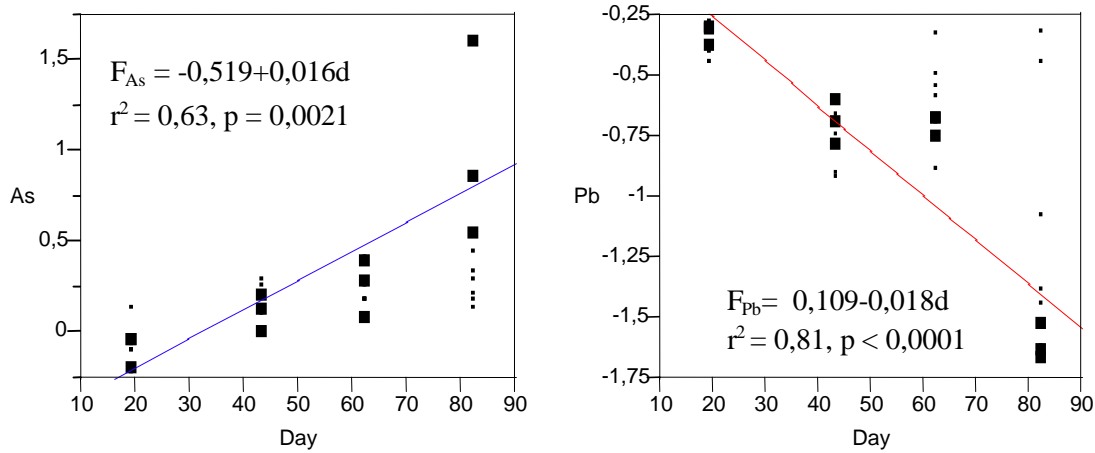


Figure 14. Trends (linear regression analyses) of total fluxes (F_T) of arsenic (left) and lead (right) from capped sediments enriched with organic matter (TOC). Small points are fluxes measured in other treatments and not included in the regression.

The initial release of Mn from the uncapped test sediment (shown by $F_{T0} > 0$) decreased ($\alpha < 0$) significantly ($p < 0,05$) during the experiment. The reduced release of As from uncapped sediments (T) provided a second example on flux changes which were not consistent with increased bioturbation, as well as the decrease of the uptake of Cd from the capped treatments (TC, T and C) ($F_{T0} < 0$, $\alpha > 0$).

Conclusively, the trend analyses showed several cases of significant flux changes which could not be explained by bioturbation. The observed changes were more likely explained as system equilibration from an unbalanced initial state towards dynamic steady states in which the fluxes are driven by solid phase equilibria in the sediments and diffusion gradients. The consequences are of some importance for the overall objective of the present investigation. In assessment of the mean flux and effects of capping, the fluxes measured in the beginning of the experiment are probably less representative for the long term fluxes than those measured towards the end of the study.

4. Conclusions and recommendations

Main results

The experiment showed significant release of Zn, Se, Cu, As, Ni, Cd and Pb from uncapped test sediments varying between 0.43 and 1730 kg km⁻² y⁻¹. The fluxes of the most bioavailable fraction of the same metals determined on DGT-samplers were between 0,013 and 593 kg km⁻² y⁻¹. From capped test sediments, fluxes were rarely significantly different from zero, yielding cap efficiencies (flux reductions) of 96% or more. Lower cap efficiencies of 89-98% were found for Mn. Neither uncapped nor capped test sediments showed any significant release of Hg, Cr and Fe. Following the above recommendations, the granular dolomite/limestone cap appears well fit for remediation purposes.

Precautions

It is important to recognize that experimental work can never fully represent all aspects of the real world. In this experiment, current velocities and exchange rates of the overlying water was small compared to the conditions at the remediation site. Advective flows in the pore water resulting from possible hydrostatic pressure variations in the shoreline environment were disregarded as well as the annual variations in light and temperatures. Water quality of the experimental water was similar to that of the St. Lawrence river with regard to pH and total concentrations of e.g. Zn and Pb, but a detailed comparison e.g. with regard to organic ligands has not been done.

The most severe concern with regard to the representativity of the results of this experiment was the short time span of the experimental period and the fact that slow changes of the chemical environment in and below the cap may decrease cap efficiencies with time.

Internal processes observed within the cap layer by the use of DGT-probes, did indicate a potential risk of spreading of copper, lead, zinc and nickel from pyrite cinders exposed to reducing conditions below the cap. The problem was only observed in carbon enriched test sediments and did not materialise into any severe release of metals to the watermass during this three-month experiment. It is recommended though, that actions are taken to reduce the risk of upwards migration of toxic metals from redox-boundaries in the cap layer.

Recommendations

The following recommendations are based on the results from this study primarily.

- Metal fluxes between the contaminated sediment and the river water will be efficiently reduced by a two-layered cap with a coarser type on top of a more fine-grained quality.
- Cap thickness of 50cm of which a lower layer of about 20cm is considered appropriate for preventing leakage of metals through the cap.
- The purpose of the lower layer is to slow down upwards diffusion of metals from the contaminated sediment.
- The purpose of the top layer is to prevent erosion of the fine grained cap and to allow maximum downwards penetration of oxygen from the river water and thereby suppress upwards migration of redox boundaries within the lower layer.
- Animals are rarely found to be active at sediment depths exceeding 5cm. The two layers are therefore considered more than sufficient to prevent the cap from biological perforation.
- Good water circulation over the capped area is beneficial due to suppression of redox boundaries.
- Geotextiles may be usefull in maintaing separation between the particles in the different layers, but will presumably have little effect on metal fluxes within the cap. Geotextiles must be completely and permanently anchored throughout the capped area.

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Appendix A. Specifications of cap material



FRANZEFOSS KALK AS

VHB 5.14.09
01.12.96/17.01.03
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KALKDOLOMITTMEL HK

Hovedelementer	Gjennomsnitt	Standardavvik	Metode
CaCO ₃	84,5 %	5,0 %	XRF – Røntgenspektrograf
MgCO ₃	7,7 %	1,0 %	XRF – Røntgenspektrograf
CaCO ₃ ekvivalenter	93,5 %	3,0 %	Omregningsfaktor
CaO ekvivalenter	51,5 %	2,6 %	Omregningsfaktor
Fe ₂ O ₃	0,6 %	0,01 %	XRF – Røntgenspektrograf
Al ₂ O ₃	1,7 %	0,2 %	XRF – Røntgenspektrograf
P ₂ O ₅	0,04 %	0,01 %	XRF – Røntgenspektrograf
Glødetap	39,7 %	0,8 %	XRF – Røntgenspektrograf
NV _{CaCO3} (kun K-mel Fin)	89	± 3	Våtkjemisk

Sporstoffer	Maks verdier	Metode
Hg	< 0,01 mg/kg*	CVAAS
Pb	< 3,0 mg/kg	GFAAS
Cd	< 0,08 mg/kg	GFAAS
Cr	< 10 mg/kg	ICP-AES
Zn	< 10 mg/kg	ICP-AES

De prosentvise verdiene må betraktes som veiledende. Råmaterialet er et naturprodukt med variasjoner i forekomsten innenfor visse grenser. Gjennomsnittsverdi ± 2 standardavvik angir hvor en finner 95% av alle målingene. * angir nedre deteksjonsgrense.

Fysiske egenskaper og landbruksverdier

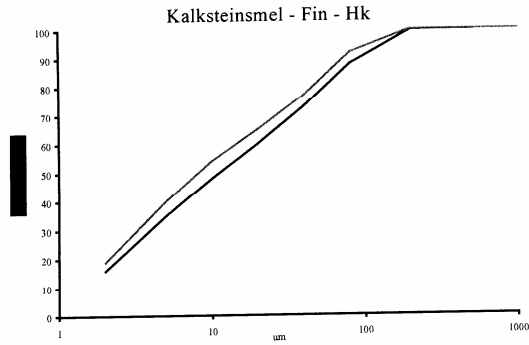
Gradering	Produkt navn	Volumvekt	Leveringsalt.	Mg + Ca- innhold	Veil. kalkverdi	pH- verdi
0 - 75 µm	Kalksteinsmel - Fin HK, Vassdragsfiller	ca 1100 kg/m ³	Bulk og 40 kg sekk	Tørr ; 3,0 % Mg 5% H ₂ O ; 2,9 % Mg Tørr ; 33 % Ca	Tørr ; 53/53 Fuktet ; 50/50	8,7
0 - 1 mm	Kalksteinsmel - Grov HK	ca 1150 kg/m ³	Bulk og 40 kg sekk	Tørr ; 3,0 % Mg 5% H ₂ O ; 2,9 % Mg Tørr ; 33 % Ca	Tørr ; 51/53 Fuktet ; 49/50	8,7
3 - 8 mm	Gytegrus 3-8 mm HK	ca 1500 kg/m ³	Bulk og Storsekk			8,7

Krystallinitet: Krystallinsk Densitet: 2,68 - 2,71 g/cm³ Hardhet (Mohs): 3



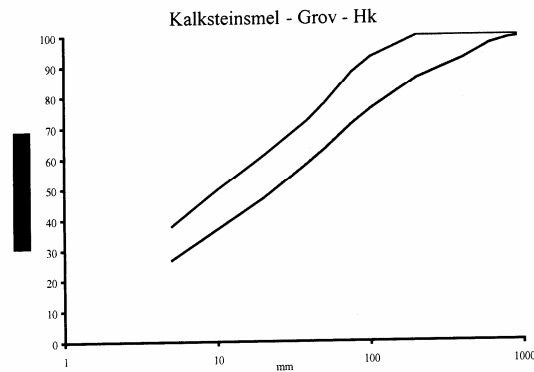


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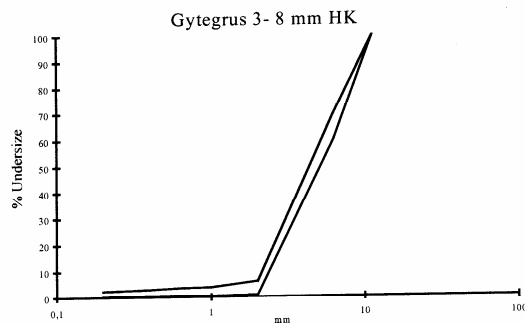
Partikkelstørrelse	Kalksteinsmel - Fin - HK
< 2 µm	16 – 19 %
< 5 µm	35 – 40 %
< 10 µm	48 – 54 %
< 20 µm	60 – 65 %
< 40 µm	73 – 77 %
< 80 µm	88 – 92 %
< 200 µm	99,8 – 100 %

Veiledende



Partikkelstørrelse	Kalksteinsmel - Grov - HK
< 5 µm	27 – 38 %
< 20 µm	47 – 61 %
< 50 µm	63 – 78 %
< 100 µm	76 – 93 %
< 200 µm	86 – 99,9 %
< 400µm	92 – 100 %
< 800 µm	99 – 100 %

Veiledende



Partikkelstørrelse	Gytegrus 3 - 8mm - HK
< 0,2 mm	0,3 – 2,5 %
< 0,4 mm	0,6 – 3 %
< 0,6 mm	0,7 – 3,5 %
< 1,0 mm	0,4 – 3,8 %
< 2,0 mm	0,8 – 6 %
< 6,3 mm	60 – 70 %
< 11,2 mm	100 %

Veiledende