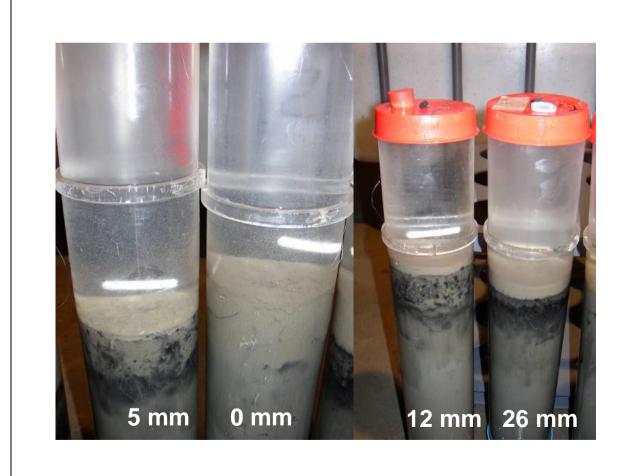


REPORT SNO 4946-2005

Environmental impacts of water based drilling mud – a pilot study



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A pilot test on waterbased drilling mud has been performed at NIVAs Marine Research Station at Solbergstrand. 15 cores with different thickness of drill cuttings were incubated for a period of 25 days, during which O₂ consumption and nutrient fluxes (NO₃ and SiO₂) were determined and microgradients studied using microelectrodes and a DGT (Diffusive Gradients in Thin-films) -probe. The results showed peak consumption of O₂ 2-15 days after addition of the cuttings. Maximum O₂ consumption was about three times higher than untreated control sediments. A general correlation was found between thickness of the cuttings layer and consumption of O2 and NO₃. Release of silicate, however, decreased in cores with layers exceeding 3-5 mm. The microelectrode showed no H₂S in the core investigated, but compared to untreated control sediments, the cuttings had reduced oxygen penetration from 5 to 3 mm depth and lowered redox potentials in the anoxic layer from ca 200 to ca 80 mV. The DGT-gradients indicated upwards diffusion of iron (Fe), lead (Pb) and barium (Ba). Fe was retained in the sediment by oxidation and precipitation at the lower boundary of the oxic layer. No evidence was found for any release of metals from the cuttings added. The recommendation for the EXPAC project was that in order to avoid severe effects of hydrogen sulphide toxicity and smothering, it is recommended not to use doses exceeding 3 mm layer thickness

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Environmental impacts of water based drilling mud

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a pilot study

Preface

This report has been prepared on request from Akvaplan-niva AS. The report is based on results from a four-week simulated seabed study performed in the soft-bottom mesocosm at Marine Research Station Solbergstrand. A preliminary report with main results on oxygen comnsumption and nutrient fluxes was distributed to Akvaplan-niva AS 16.02.04. The experiment used undisturbed sediment communities transferred to the mesocosm from 35 m depth in the Oslofjord using RV Trygve Braarud, Oslo. All samples were analysed at NIVAs laboratories accredited according to NS-EN ISO/IEC 17025. We thank the crew on RV Trygve Braarud and Frode Olsgard (NIVA) for collecting the sediment samples. All NIVA-personell involved at Marine Research Station Solbergstrand and in the laboratory in Oslo is acknowledged for their contributions.

Oslo, 28.01.05

Morten Schaanning

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Summary

Effects of increasing layer thickness of drill cuttings on oxygen consumption and nutrient fluxes were investigated in 15 cores with Oslofjord sediments incubated in a flow-through system with seawater of 34 PSU and 7°C. The cuttings were sampled from an off-shore drilling operation with water-based mud and added to the cores on day 0 in layers with calculated layer thickness ranging from 0,4 to 32 mm.

A large, but narrow peak of oxygen consumption was observed in high dose treatments 1-2 weeks after addition of the cuttings and indicated the presence of a small amount of a highly degradable organic phase. A significant correlation was found between nitrate and oxygen consumption, but the release of silicate was clearly reduced at layers exceeding 3-5 mm, probably as a result of slow mineralization of silicate in the cuttings, reduced ability of the bioturbators to penetrate thicker layers and possibly also increasing sulphide toxicity in the thicker layers.

Production of H₂S was indicated by black spots and layers developing during the incubation period in the sediments immediately below cuttings layers with thicknesses of 1 mm or more. Black spots were not detected neither in control cores nor within the cuttings layers themselves. The latter was argued to result from slow production of ferrous iron within the cuttings layers, but more complex explanations involving microbial heterogeneity should not be ruled out.

Microgradients were investigated in one core 3 weeks after the addition of 1,5 mm cuttings. The microelectrodes showed no H_2S in the core investigated, but compared to untreated control sediments, the cuttings had reduced oxygen penetration from 5 to 3 mm depth and lowered redox potentials in the anoxic layer from ca 200 to ca 80 mV. The DGT-gradients indicated upwards diffusion of iron (Fe), lead (Pb) and barium (Ba). Pb and Ba appeared to be released across the sediment water interface, but Fe was retained in the sediment by oxidation and precipitation at the lower boundary of the oxic layer. No evidence was found for any release of metals from the cuttings added.

If effects of hydrogen sulphide toxicity and smothering is to be considered as bias in the main project, it is recommended not to use doses exceeding 3 mm layer thickness.

1. Background and objectives

After the ban on discharge of oil based muds in the Norwegian sector of the North Sea at about 1990, the Norwegian Instute for Water Research has developed the so-called Simulated Seabed Study for assessment of degradation rates and effects on benthic communities of cuttings deposited in the marine environment (Bakke et al., 1989, Berge, 1995, Schaanning and Bakke, 1997, Schaanning et al., 1997, Schaanning and Rygg, 2002). On request from the oil industry, a number of tests have been performed on OBMs (oil based muds) and muds based on substitute organic phases such as esters, ethers and olefins, often referred to as SBMs (synthetic based muds).

This study has been performed on request from Akvaplan-niva AS as a pilot test for the EXPAC-project. The objective of the pilot test has been to determine the relationship between dose (layer thickness) of the most frequently discharged WBMs (Water Based Muds) and bentic metabolism. The set-up and variables determined in this experiment was designed for different purpose and deviates in many respects from the set-up used in previous tests. The main difference is the shorter test duration (4 weeks vs six months), the smaller experimental units (0,008 m² cores vs 0,1 or 0,25 m² box cores) and the study performed on microgradients using new techniques such as microelectrodes and DGT-probes.

2. Methods

2.1 Collection of test communities

Undisturbed benthic communities were collected at about 35 m depth in Bjørnhodebukta in the Oslofjord. Cores were collected from RV Trygve Braarud, Oslo, using a Bowers and Connolly multicorer which takes 4 undisturbed sediment samples in transparent acrylic tubes (10 cm diameter, 60 cm high). A well oxygenated layer of seawater was always present on top of the sediment in the cores and salinity and temperature similar to the ambient conditions at the sampling location was maintained throughout transportation.

2.2 Set-up

All cores were installed in the mesocosm laboratories at Solbergstrand Marine Research Station the same day as they were collected. The cores were incubated in water bath continously flushed with seawater supplied from the Oslofjord at 60 m depth (Figure 1). Each core was continously supplied with an accurate flow of seawater (60 m), using a Watson-Marlow multichannel peristaltic pump. Each core had a rod magnet hanging in overlying water 2-3 cm above the sediment surface. The rod magnet was hanging in a fishing line adjustable through the lid of the cores. Remotely controlled "door lock" magnets were attached on the outside of each core. From an electronic control unit the external magnets were triggered every 3 seconds to attract the rod magnets. This caused the magnet rods to be attracted against the wall of the cores in pulses of 3 seconds, causing the motion required to break down any stratification in the core water. The system was used for simultaneous stirring in 18 cores and maintained a perfectly stable stirring throughout the four-week experimental period.

The day after collection the water supply and the stirring was stopped and the test product was added to the cores. The test product (mud) was delivered from Statoil (West Navigator, Statoil, Well 6507/3-4). The mud was mixed with water into a slurry (mixing ratio 1:1) using a high-speed stainless steel mixer used for sediments only. The slurry was poured into the cores in 12 doses, from 6 to 720 grams yielding calculated layer thickness from 0,38 to 45,8 mm (Table 1). Three cores with undisturbed sediment were used as control, and 3 more cores were kept for backup.

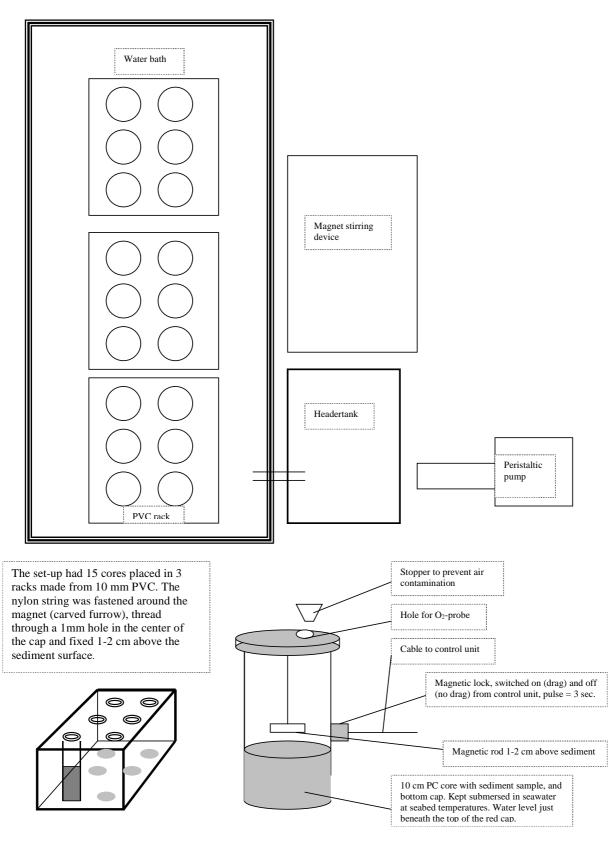


Figure 1. Test set-up.

Table 1. Added amount of slurry to each core. The slurry was made up by mixing cuttings and seawater 1:1 by weight. Mixing was performed in a stainless steel "cocktail mixer" with high speed propeller. Thickness measured at termination of experiment.

propener. Thickness measured at termination of experiment.						
		Measured				
		thickness				
Added slurry (g)	Calculated layer thickness (mm)	(mm)				
6	0,382	1				
11,9	0,757	1				
24,2	1,539	2				
48,5	3,085	5				
95,9	6,099	10				
144,1	9,165	12				
191,9	12,205	14				
239,8	15,252	26				
359,9	22,890	26				
480	30,529	45				
600	38,161	53				
720	45,793	65				

2.3 Sampling and analyses

2.3.1 Sample collection

After addition of the slurries, the cores were left for a few hours before circulation pumps were started for continuous exchange of the head-space water. Oxygen consumption measurements were performed the next day (day 0) and repeated at 1-3 times per week during the next 25 days. Nutrient fluxes (nitrate and silicate) was measured on day 12, 18 and 25.

On day 20 microprofiles were determined in one control core and the core treated with 1,5 mm calculated layer thickness. The cores were mounted on a laboratory stand and electrodes were inserted at 1 mm intervals using a manually controlled micromanipulator. Measurements were taken from 5 mm above the sediment-water interface down to 20 mm sediment depth.

On day 25-26, a DGT-probe was deployed for 24 hours in the core treated with 1,5 mm cuttings. The probe extracts metals from the surrounding medium onto an ion exchange resin through a 15 cm high "window". The "window" was positioned vertically across the sediment water interface. After retrieval and rinsing, the probe was sliced in 2,5 mm sections. Sections from the depth interval between 10 mm above and 35 mm below the sediment water interface were eluated and analysed for several metals including Ba, Ti, Fe, Mn, Ni, Cu, Pb, Cd, Zn, Co, V and Cr.

Chemical analyses of nutrient species and metals were performed at NIVAs laboratories in Oslo which are accredited in accordance with international standards NS-EN ISO/IEC 17025.

2.3.2 Flux measurements

Fluxes of oxygen (O_2) and nutrient species (NO_3 and SiO_2) were determined by successive measurements of concentrations in the inlet water and in the well mixed water above the sediment in each core. O_2 differences were measured with a precision <0,05 mg O_2 l⁻¹ using an oxygen electrode. Water samples were drawn from the header tank and each chamber using a 50 ml syringe. The syringe

was rinsed with sample water before transfer of subsamples to separate vials for each nutrient and preserved using 1 ml 4M $\rm H_2SO_4$ per 100 ml sample for $\rm NO_3$, and 2 drops of chloroform per 20 ml sample for $\rm SiO_2$. All samples were stored in the dark at -20°C untill analyses at the NIVA-laboratory using automated spectrophotometric methods for nutrient analyses in sea water based on NS 4745, and Technicon autoanalyser (Grasshoff et al.1985).

Fluxes were calculated from the equation:

$$\mathbf{F} = (\mathbf{C}_{i} - \mathbf{C}_{o}) \cdot \mathbf{Q} \cdot / \mathbf{A}$$

in which

F is the flux (μ mol m⁻²h⁻¹) C_i is the concentration in the headertank C_o is the concentration in the respective core Q is the flow of water through the respective core A is the area of the core

The flow of water through each core was measured gravimetrically after collection of outflow water for 5 minutes.

2.3.3 Microelectrodes

Unisense microelectrodes (OX-50, PH-100, H2S-50, RD-100, REF-5000) were used to determine microgradients of oxygen, pH, redox potential and sulphide ion concentration in the sediment-water interface. The microelectrodes are fast-responding and provide a spatial resolution of two times the tip diameter (Revsbech 1989). After calibration, the electrodes and the core to be measured were mounted on a LS18 laboratory stand (Figure 2). The electrodes were inserted into the overlying water and sediment using a manually controlled micromanipulator. Measurements were done in 1 mm intervals from 5 mm above the sediment-water interface down to 20 mm sediment depth. The OX-50 and H2S-50 electrodes were connected to a picoammeter, while pH and redox electrodes were connected to a high impedance millivolt meter during measurements. The readings were transferred from the picoammeter and millivoltmeter to an online-pc. The pH and redox electrodes were used together with a reference electrode.

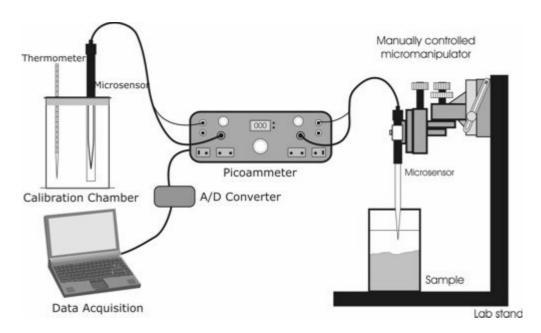


Figure 2. Microelectrode set-up.

O₂ measurements

For O_2 -measurements a Clark-type OX-50 microelectrode equipped with an internal reference and a guard cathode were used (Revsbech, 1989). This electrode has tip diameter of 50 μ m, stirring sensitivities of <1% and a 90% response time of <1 s (Revsbech 1989). Before measurements a two-point calibration was performed in, respectively, oxygen-free water obtained by bubbling with inert gas e.g. N_2 and well aerated water.

Sulphide measurements

For sulphide measurements a Clark-type H_2S -microelectrode equipped with an internal reference was used (Unisense H2S-50). H_2S from the surrounding environment penetrate the sensor tip membrane into the alkaline electrolyte, where the sulphide is immediately oxidized by ferricyanide, producing sulfur and ferrocyanide. The sensor signal is generated by re-oxidation of ferrocyanide at the anode in the tip of the sensor (Jeroschewski et al. 1996). The H_2S microsensor responds linearly over a certain range (e.g. 1-300 μ M).

Before measurements an 8 point calibration was done. An S^{2-} stock solution of 0,028 M (total sulphide) was prepared by dissolving 0,629g Na₂S(H₂O)₇₋₉ in 100mL of N₂-flushed water in a closed container. The calibration curve was obtained by addition of aliquots (0,1 ml at a time, 8 times) of the S^{2-} stock solution anaerobically into 100 ml pH buffer (pH=7). The calibration curve is shown in figure 3.

pH-measurements

pH-measurements were done using a Clark-type Unisense PH-100 pH-microelectrode together with a reference-electrode (Unisense REF-5000). The PH-100 microelectrode has a tip diameter of 90-100 μ m and is based on selective diffusion of protons though pH glass, and the determination of potentials between the internal electrolyte and a counter electrode. The pH-electrode was connected to a high impedance milivolt meter which read the signal from the pH electrode during measurements. Prior to the sediment measurements a two-point calibration was performed in standard phosphate pH buffers (4 and 7). The pH microelectrode respond linearly with a slope of 50-70 mV/pH-unit. The millivolt-readings during measurements in sediments were converted into pH-values using the calibration values.

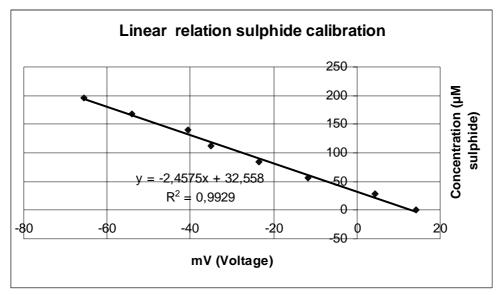


Figure 3. Calibration curve for sulphide.

Redox potential measurements

Redox potentials were measured using a Clark-type Unisense RD-100 redox microelectrode together with a reference-electrode (Unisense REF-5000) The RD-100 microelectrode is a miniaturized redox platinum electrode with a tip diameter of 100 μm and a response time of 90 % in less then 1 sec.. When the electrode tip is immersed in an aqueous solution and connected via a high-impedance millivoltmeter to a reference electrode immersed in the same solution, the redox electrode tip develops an electric potential relative to the reference electrode which reflects the tendency of the solution to release or take up electrons (Oxidation-Reduction Potential). Prior to measurements a two-point calibration was performed in saturated quinhydrone buffer solutions with E_h of respectively 385 mV and 486 mV at 10 °C. The potentials measured in the buffers showed an off-set potential of 160 mV which should be added to the potentials recorded in the sample to obtain the correct E_h against the standard hydrogen electrode.

2.3.4 DGT -probe

A DGT (Diffusive Gradients in Thin-films) probe was deployed for 24 hours in a sediment core with 24 g slurry added. The sampler collect metal ions on an ion exchange resin packed beneath a thin gel through which free or losely bound metal ions can diffuse. After deployment for 24 hours, the DGT unit was removed from the sediment, rinsed with dest. H2O and dispatched for processing under controlled conditions in NIVAs laboratory. The probe material was sliced into 2,5 mm thin slices, eluted with acid and analysed. The mass of metals accumulated per unit area of the resin layer was measured using ICP-MS.

3. Results and discussion

3.1 Sediment appearance

The sediments in all control cores maintained a homogenous light gray appearance (Figure 4) throughout the experiment. Surprisingly, also the cuttings layers maintained a similar light gray colour, whereas blackening of the sediments was observed immediately below the cuttings layer in all cores treated with cuttings. Black spots were observed below cuttings layers as thin as 1 mm. Below cuttings layers of 10 mm and more, homogenous blackening was observed penetrating downwards to several cm below the cuttings layer. The blackening was assumed to result from rapid sulphate reduction of some organic phase within the cuttings layer. The H₂S produced will then diffuse downwards into the underlying sediments within which black ferrous sulphides precipitated. The absence of black precipitates within the cuttings layers may be due to absence of significant amounts of ferrous iron available for precipitation. Other explanations involving the distribution and activity of sulphate reducing or other heterotrophic bacteria should not be ruled out.

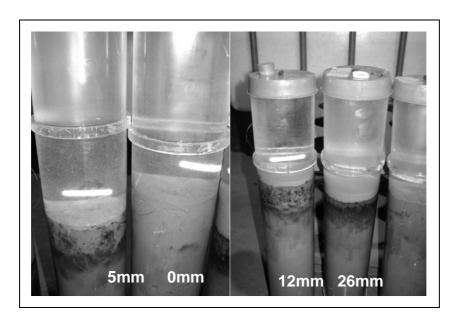


Figure 4. Photos taken by end of experiment of cores treated with respectively 0, 5, 12 and 26 mm layers of cuttings.

3.2 Oxygen consumption

In the headertank (source water) concentrations of O_2 varied between 9 and 11 mg O_2 Γ^1 . In the cores, the concentration was lower and whenever the concentration decreased to less than 50% of the source water, flow was increased. Thus concentrations in the cores were typically about 5-8 mg O_2 Γ^1 , with a minimum of 2,66 mg O_2 Γ^1 recorded in one of the high dose cores on day 5, before flow regulation.

The temperatures in the header tank varied between 6,9 and 7,1°C. In control cores oxygen consumption increased from about 600 μ mol m⁻² h⁻¹ on day 0 to about 1600 μ mol m⁻² h⁻¹ after two weeks. During the last two weeks of the experiment oxygen consumption remained at this high level. The increase was probably a result of bacteria growing on the inside surfaces of cores and tubes, which in the present set-up was relatively large compared to the area of sediment surface.

In most of the cores with thick layers of wet cuttings, i.e. 15, 23, 31 and 46 mm, oxygen consumption showed a large peak 8-12 days after addition of cuttings (Figure 5). In the cores with thin layers, i.e. 0.4-12 mm, oxygen consumption showed a small peak on day 2, but about ten days after addition of cuttings a cross-over was observed to yield O_2 consumption lower than control in most of these cores during the last two weeks of the experiment. It appears reasonable to relate this cross-over to the increase of SOC in control cores, indicating less bacteria growth on the walls in cores treated with cuttings. The dual peak in oxygen consumption rates may result from microbial succession with strong dominance of sulphate reducers and chemical consumption of O_2 by the H_2S produced to yield the large peak at day 8.

Integrated over the whole 25 days period (Figure 6), oxygen consumption was 704,6 mmol m⁻² in the control cores with a standard deviation of 17,6 mmol m⁻² (n=3). The highest SOC of 1418 mmol m⁻² occurred in the core with 23 mm cuttings layer. The SOC of two cores with the lowest dose of cuttings were not much different from control quite similar to control in all cores with layers less or equal to 12 mm. The correlation between dose added and cumulative SOC for the whole period (Figure 7) was not very good with a correlation coefficient $r^2 = 0.416$, but the relationship was significant (p = 0.0175).

3.3 Nutrient fluxes

Fluxes of NO_3 and SiO_2 were measured after 12, 18 and 25 days. The results are shown in Figure 9-Figure 12. Nitrate was always consumed in the cores and consumption rates were reasonably well correlated with dose of cuttings (Figure 11) and consumption rates for oxygen (Figure 8). Silicate was released in all sediment cores. The rates increased sharply with increasing dose up to 3 mm (Figure 10, Figure 12), but beyond this dose the release of silicate was often lower than control and tended to decrease with increasing layer thickness. The release of silicate from Oslofjord sediments is often well correlated with oxygen consumption, but different from O_2 and NO_3 which are directly used as electron acceptors by heterotrophic bacteria, SiO_2 is released from dissolution of silicate minerals and skeletons. The collapse of the silicate flux in the present cores at layer thickness >3 mm, was probably a result of slow silicate mineralization in the cuttings layer and physical inhibition of the diffusion and bioturbation driven flux from the sediments beneath the cuttings layer. The apparent threshold value at 3-5 mm may be related to the ability of the present fauna to penetrate a particle layer. Increasing concentrations of sulphide may have contributed to reduce the penetration ability by biochemical inhibition of bioturbating organisms.

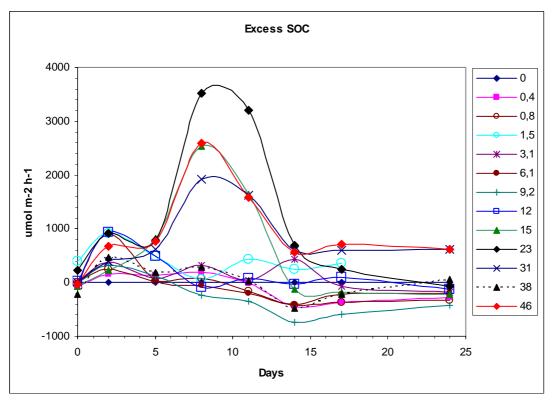


Figure 5. Excess sediment oxygen consumption (treated-control). Legend shows calculated thickness (mm) of wet cuttings layers.

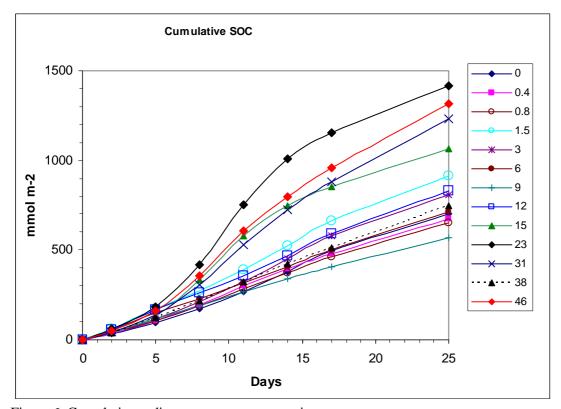


Figure 6. Cumulative sediment oxygen consumption.

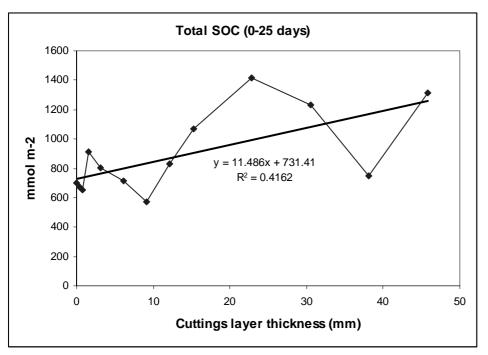


Figure 7. Linear regression of O₂ consumption rates vs dose for day 8.

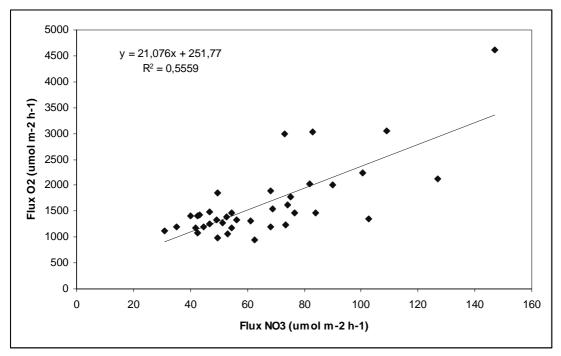


Figure 8. Linear regression between fluxes of O₂ and NO₃.

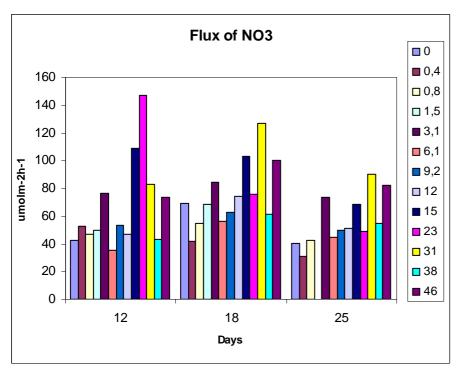


Figure 9. Fluxes of NO₃ determined 12, 18 and 25 days after addition of drilling mud. Legend shows calculated thickness (mm) of wet cutting layer. Positive flux shows uptake in sediment.

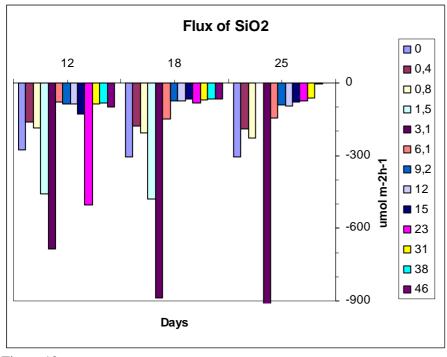


Figure 10. Fluxes of SiO_2 determined 12, 18 and 25 days after addition of drilling mud. Legend shows calculated thickness (mm) of wet cutting layer. Negative flux shows release from sediment to water.

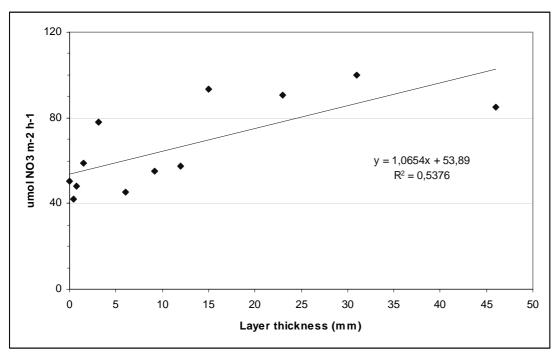


Figure 11. Mean flux of NO₃ vs dose and linear regression curve fit.

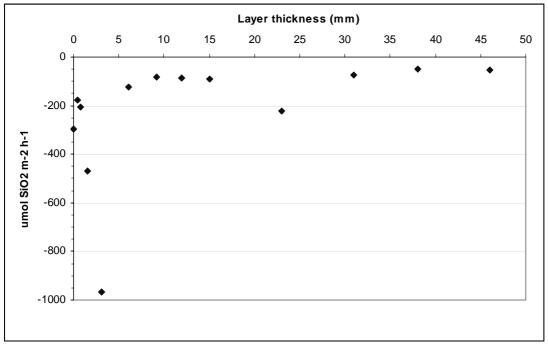


Figure 12. Mean flux of silicate vs dose.

3.4 Microelectrode-studies

Pore water investigations of pH, redox, oxygen and sulphide were done on two sediment cores. One control core without cuttings added and one sediment core with 24 g slurry added (1,5 mm thick layer). Figure 13 shows the sediment pore water profiles.

In the control sediment the oxygen penetrated to 6 mm depth. In the core with cuttings added, oxygen penetrated 2-3 mm into sediment. The microsensor measurements in the water above the sedimentwater interface showed lower oxygen saturation in the sediment core with cuttings added (ab. 30 %) compared to the control core (ab. 60%). This confirmed that oxygen is used for decomposition of cuttings.

Redox-potentials decreased from the sediment-water interface and down into the sediment. The sediment core with cuttings had generally a lower redox-potential both in the water and pore water compared to the control core, and a steeper gradient beginning just below the cuttings layer. This profile might result from degradation within the sediment and reduced exchange across the cuttings layer (lid effect). However, considering the fact that the measurements were performed about two weeks after the degradation event (Figure 5), the observed profile is probably best interpreted as a stage in the successive remediation after the degradation event. The lowering of the E_h was primarily driven by degradation in the cuttings layer and subsequently transferred to deeper layers. When degradation slows down, diffusive exchange with the overlying water will restore more normal E_h -values close to the sediment-water interface leaving the most disturbed conditions at larger depths in the sediment.

The proliferation of black spots during the degradation event indicated that sulphate reduction had contributed to the rapid degradation of the organic phase. By the time of the microelectrode measurements, concentrations of sulphide were below detection limits (Figure 13). Sulphide will be rapidly depleted by reactions with free oxygen (upper 2-3 mm sediment depth) and mineral phases present in the sediment. The absence of O2 and H2S, but presence of dissolved iron, probably Fe2+ions, was consistent with intermediate redox potentials.

The pH-profile showed only small variations at the sediment-water interface.

3.5 DGT-profile

Metals adsorbed within 2,5 mm depth intervals of DGT-probes during 24h deployment in one core are shown in Figure 14. Of the metals analysed in this study (appendix 1) only iron (Fe) and lead (Pb) showed clear gradients in the DGT. The Barium (Ba) profile showed several large "kick-backs", but a general increase with depth throughout the measured layer and a steady increase across the sediment water interface tend to suggest a general efflux of Ba from the sediment. The profile gave no evidence, however, that the cuttings acted as a source of Ba available for uptake on the DGT-probe.

The lead concentration increased from $0.05 \,\mu\text{g/l}$ DGT extract in the sediment-water interface to $0.12 \,\mu\text{g/l}$ DGT extract at 5 mm sediment depth. This indicated a flux of lead from the sediment to the overlying water, but again the profile gave no evidence that the cuttings added acted as a source of the Pb-efflux. The iron concentration showed no increase at the sediment-water interface, but started to increace from 9 $\mu\text{g/l}$ DGT extract at 3 mm sediment depth to 58 $\mu\text{g/l}$ DGT extract at 8 mm sediment depth. This indicated that iron was retained in the sediment by oxidation of upwards diffusing Fe²⁺-ions at 3 mm depth at which oxygen from the watermass becomes available (Figure 13).

The observed DGT-profile gave no evidence for any release of metals from the cuttings added.

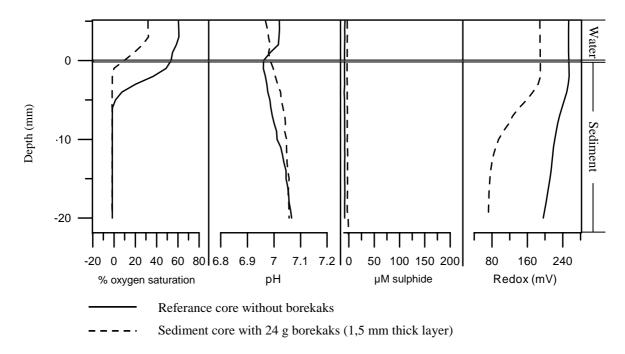


Figure 13. pH, sulphide, oxygen and redox microprofiles.

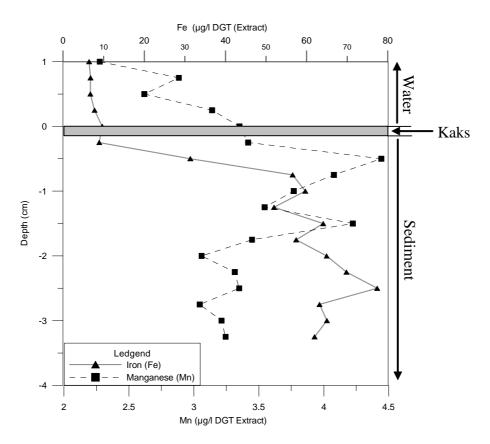


Figure 14. Iron and manganese DGT-profiles from sedimentcore with 24 g slurry (1,5 mm thick layer).

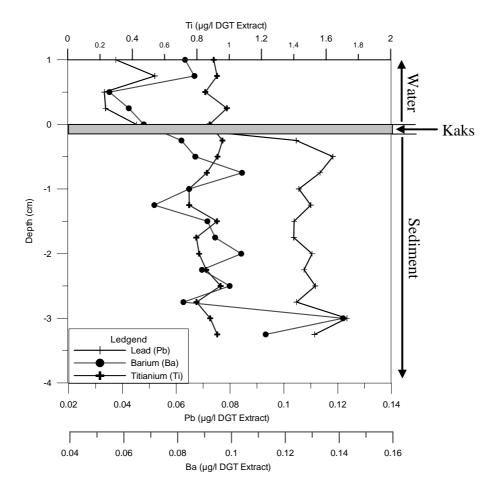


Figure 15. Titanium, barium and lead DGT-profiles from sedimentcore with 24 g slurry (ca 1,5 mm thick layer).

4. Conclusions

Addition of waterbased cuttings initiated a short event of increased oxygen and nitrate consumption and the formation of black sediments below the cuttings layer. These observations showed that the cuttings supplied contained a small amount of an organic phase highly available for the heterotrophic sediment community including sulphate reducing bacteria.

The release of silicate was inhibited at cuttings layers exceeding 3-5 mm.

Concentration gradients measured on a DGT-probe indicated a general release of lead and barium from the sediment, but no evidence was found that the cuttings layer was a source for release of any metal.

Microelectrodes showed that three weeks after addition of a 1,5 mm thick layer of cuttings, dissolved O_2 penetrated down to 3 mm depth as compared to 5 mm depth in an untreated control core. In the same two cores, the redox potential below the oxic layer had been reduced from about 200 mV in control to about 80 mV in the core with cuttings added.

If effects of hydrogen sulphide toxicity and smothering is to be considered as bias in the main project, it is recommended not to use doses exceeding 3 mm layer thickness.

5. References

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Appendix A. DGT analyses

Unit: µg/l DGT extract

De al (con)	D. (. /T.)	M. (./II)	A1 (- ///)	C (T)	TD* (. /TC)	X 7 (. / T)	C (T)	M. (. T.)	Fe
Depth (cm)	Be (ug/L)	Mg (ug/L)	Al (ug/L)	Ca (ug/L)	Ti (ug/L)	V (ug/L)	Cr (ug/L)	Mn (ug/L)	(ug/L)
1.00	0.02084	1632	1.774	707.6	0.9039	0.03015	0.05017	2.275	6.371
0.75	0.02458	1784	1.794	791.6	0.9242	0.02231	0.08054	2.885	6.741
0.5	0.00829	1489	1.117	678.3	0.8518	0.02226	0.07054	2.619	6.699
0.25	0.00834	1632	1.438	755.5	0.9854	0.01878	0.06482	3.140	7.749
0.00	0.01634	1533	1.629	722.1	0.8785	0.02138	0.07293	3.351	9.610
-0.25	0.02099	1528	1.569	711.1	0.9579	0.03321	0.07065	3.418	8.892
-0.5	0.02058	1485	1.599	711.3	0.9272	0.04885	0.07487	4.444	31.35
-0.75	0.01313	1404	2.342	631.2	0.8614	0.04344	0.0873	4.078	56.56
-1.00	0.02503	1256	1.777	596.2	0.7518	0.04605	0.07112	3.770	59.69
-1.25	0.00405	1210	2.306	570.9	0.7526	0.04464	0.06824	3.545	51.98
-1.5	0.02130	1554	1.724	734.9	0.9242	0.05328	0.06256	4.224	64.06
-1.75	0.02128	1352	2.187	642.1	0.7966	0.03972	0.05582	3.448	57.42
-2.00	0.03360	1335	2.703	625.7	0.8129	0.04056	0.05462	3.059	64.92
-2.25	0.03947	1384	1.498	661.5	0.8571	0.04303	0.07488	3.315	69.80
-2.5	0.02607	1522	1.704	709.0	0.9463	0.04041	0.04588	3.349	77.38
-2.75	0.05225	1350	1.456	639.8	0.7976	0.04181	0.0329	3.045	63.16
-3.00	0.00444	1358	2.493	668.0	0.8819	0.05095	0.1087	3.213	64.98
-3.25	0.01287	1400	2.136	707.7	0.9258	0.04451	0.05404	3.244	61.94

Depth (cm)	Co (ug/L)	Ni (ug/L)	Cu (ug/L)	Zn (ug/L)	Sr (ug/L)	Cd (ug/L)	Ba (ug/L)	Pb (ug/L)	U (ug/L)
1.00	0.004172	0.1046	0.07972	0.6567	9.114	-0.000537	0.08276	0.03757	0.1502
0.75	0.00503	0.1434	0.09995	1.007	10.13	0.000924	0.08624	0.05206	0.1546
0.5	0.004434	0.1154	0.06092	0.5216	8.3	0.000839	0.05462	0.03326	0.1245
0.25	0.00393	0.1147	0.1033	0.4939	9.182	0.000369	0.06182	0.03372	0.1485
0.00	0.005941	0.1421	0.06326	0.6899	8.836	-0.001379	0.0674	0.04518	0.1544
-0.25	0.005432	0.1718	0.08777	0.77	8.963	0.001735	0.08142	0.1046	0.1396
-0.5	0.006589	0.1582	0.1084	1.138	8.419	-0.000425	0.08656	0.1182	0.1049
-0.75	0.008282	0.1918	0.1541	1.317	8.183	-0.000849	0.1039	0.1134	0.1014
-1.00	0.009209	0.1450	0.0691	0.8144	7.258	-0.000567	0.08428	0.1056	0.09114
-1.25	0.00972	0.1363	0.04835	0.5532	6.958	0.000496	0.07132	0.11	0.0885
-1.5	0.01278	0.1628	0.04393	0.79	8.832	0.001469	0.09102	0.1038	0.1075
-1.75	0.008408	0.1684	0.07282	0.6772	7.844	-0.00167	0.09389	0.1037	0.0925
-2.00	0.00929	0.1691	0.09609	1.013	7.907	-0.000619	0.1036	0.1105	0.09197
-2.25	0.009818	0.1589	0.03803	0.5905	8.25	-0.000594	0.089	0.1075	0.0943
-2.5	0.01109	0.1463	0.05955	0.7211	9.12	0.000509	0.0993	0.1117	0.09965
-2.75	0.008024	0.1328	0.04066	0.5577	8.09	-0.000171	0.08214	0.1047	0.08708
-3.00	0.007484	0.1576	0.09157	1.537	8.211	0.001075	0.1414	0.1234	0.08679
-3.25	0.009632	0.1738	0.09993	0.9198	8.665	0.000343	0.1127	0.1114	0.09282