O-93206

Test on Degradation of AQUAMUL BII Drill Mud on Cuttings under Simulated Seabed Conditions

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Abstract:

New, synthetic drilling fluids are exploited by the oil industry to replace mineral oil in muds for North Sea drilling operations. Aquamul BII, which is a modification of the previously tested Aquamul B, is a high purity liquid ether drilling fluid with a stoichiometry corresponding to $C_{20}H_{42}O_2$. In the present study, cuttings contaminated with a mixture of 60% BII and 40% Aquamul B ethers, were tested in benthic chambers at the Solbergstrand Marine Research Station against cuttings contaminated with mineral oil and ester based drilling muds. During the 150 days test period, sediment samples showed significantly decreasing concentrations of all drilling fluids. Estimated halflifes were 20 days for the esters, as compared to more than a year for mineral oil THC and Aquamul ethers. However, enrichment effects were much more pronounced in chambers treated with ester cuttings. It was concluded that at the deposition sites in the North Sea the choice between the ester and the ether based muds appeared to be the choice between dramatic effects over a small area of a short period of time and moderate effects over a larger area for a longer period of time.

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Cover photo shows 2-3 mm thick layer of cuttings on test sediment. Photo was taken through acrylic wall of chamber AQII-8 on day zero. Some of the larger benthic animals had crawled upwards along the wall to escape the cuttings.

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Preface

This report describe the results of NIVA project O-93206, which was performed for Saga Petroleum a.s. on request from SFT. The experimental work was done at NIVA Marine Research Station Solbergstrand (MFS) during the period September 1993 to March 1994. Frøydis Oreld and coworkers at SINTEF Department of Industrial Chemistry (SI) was subcontracted to perform the chemical analyses of the drilling fluids. Their report is enclosed in Appendix 2.

Oslo, 30. juni 1994

Morten T. Schaanning
Project Manager

Summary

Aquamul BII is a modification of the older Aquamul B drilling fluid used for substitution of mineral oil in off-shore drill muds. Whereas the Aquamul B drilling fluid consisted of a complex mixture of di-decyl ether isomers, Aquamul BII consisted of one main compound with a stoichiometry fitting the formula $C_{20}H_{42}O_2$.

The objectives of the present study was to test the biodegradation and environmental effects of Aquamul BII ethers in drill mud on cuttings deposited on sediments ressembling as much as possible the conditions at the North Sea seabed, and to compare the behaviour of the Aquamul BII cuttings to other cuttings containing Petrofree esters and mineral oil, respectively.

Unfortunately, the drilling fluid in the test material proved not to be a pure Aquamul BII, but a mixture of 60% of Aquamul BII ether and 40% of the old Aquamul B ethers. Both fluids were quantitated separately. Thus the test could yield the rate of loss of both fluids, but total mass balance and environmental effects could not be asssigned to either one of the products.

Cuttings samples were obtained from drilling operations in the North Sea. Aliquots of the cuttings were suspended in seawater and allowed to settle through a column of seawater to form thin (≈1mm) layers on top of non-contaminated fjord sediments in eight replicate benthic chambers. Thus, two chambers were treated with Aquamul BII ether cuttings, two chambers were treated with Petrofree ester cuttings and two chambers were treated with mineral oil cuttings. The last two chambers were control chambers not treated with cuttings.

The chambers were continuously flushed with Outer Oslofjord seawater taken from 40-60 m depth. At various time intervals during the 150 days experimental period, sediment samples were drawn for chemical analyses of the drilling fluids. pH and redox potentials were measured to assess the state of the benthic ecosystem and oxygen consumption was measured to assess biodegradation.

In previous tests, large variations in concentrations of drilling fluids determined in sediment samples have been a major problem for the interpretation of test results. Relative standard deviations of 50% or more of the concentration were frequently observed. In the present test, modifications of sampling strategy and implementation of other concentration units for the drilling fluids were undertaken to improve overall test reproducibilty. During this study, the concentrations of the various drilling fluids

determined in series of six parallell sediment samples, yielded relative standard deviations between 8.3% and 14.8%. This represented a major improvement with regard to test precicion.

The improved reproducibility revealed, however, that a previously recognised, suspicious increase of concentrations of certain drilling fluids during the first 1-2 months, could no longer be explained as a result of random errors. Thus, a post-depositional ageing process was hypothesised. During this ageing process, the drilling fluids became more strongly bound to sediment particles. Thus some loss of an organic phase with high affinity for the plastics in the sampling devices, was assumed to have caused a systematic underestimation of Aquamul ethers and mineral oil THC in the samples drawn on day zero.

In spite of possibly underestimated day zero concentrations of Aquamual ether and mineral oil THC, significant loss from the sediment of all drilling fluids tested, was observed during the experimental period.

The degradation curve for the Petrofree esters fitted a second order reaction model:

$$C = C_0 \cdot 10^{-kt}$$

in which C was the concentration at time t and k was the rate constant for the reaction. Regression analyses on the observed concentrations gave a rate constant, $k = 0.0148$. Thus, the half-life τ, given by the relationship $\tau = \log 2/k$, was found to be 20.3 days for the Petrofree ester which agreed closely to previous tests on this compound. The calculated regression coefficient, $r = 0.995$, showed a very good fit of the observations to this exponential model.

The degradation curves for the other drilling fluids did show significant loss, but fits to linear or exponential regression models were not so good. This was shown by regression coefficients between 0.4 and 0.6. Best fit regression curves gave half-lives of 399 days for Mineral oil THC, 392 days for Aquamul B and 536 days for Aquamul BII ethers. These estimates were rather uncertain and the longer half-life found for Aquamul BII as compared to Aquamul B and mineral oil THC might result from a higher initial concentration of Aquamul BII, rather than from a real difference in degradability.

A better description of the loss of the Aquamul ethers as well as the mineral oil THC might be derived from a model which allow an initial lag phase with slow degradation followed by a linear or exponential loss of the drilling fluids. At initial doses of about 5 $mg \cdot cm^{-2}$, the length of such lag phases appeared to be 1-3 months. In the present study, most of the loss of the Aquamul ethers and mineral oil THC was observed to occur

between day 60 and 120. If a prolonged study had shown that the increased loss rates observed at about three months continued untill degradation was complete, half-lives might prove to be shorter than those calculated above.

In the process of biodegradation the organic carbon in the drilling fluids are ultimately oxidised to CO_2. The amount of carbon converted to CO_2 can be estimated from the oxygen consumed. Thus, simultaneous measurements of loss of drilling fluids and oxygen consumed, may be compared to assess remineralisation versus other loss.

Assuming that day zero concentrations of THC were slightly underestimated, the present experiment showed that the amount of carbon mineralised to CO_2 could account for 98% of the total loss of THC. This showed that the mineral oil had been confined to the sediment surface for at least 150 days after deposition. Negligible amounts had been lost to the watermass by resuspension of particles or leakage of soluble metabolites. Neither had bioturbation provided any significant loss by burial of mineral oil THC to below the sampling depth of two cm. Approximately 30% of the added THC had been lost by slow remineralisation to CO_2.

Corresponding budgets calulated for Aquamul ethers and Petrofree esters showed that complete remineralisation to CO_2 could account for no more than 20-40% of the observed loss of Aquamul ethers and 44-47% of the loss of Petrofree esters. It appeared unlikely that leakage to the watermass or any other physical process acting on the ether and ester compounds could account for the remaining loss.

However, the decomposition of these synthetic fluids are likely to begin with an enzymatic hydrolyses splitting the molecules at the carbon oxygen bonds. The products of the ester hydrolyses should be a mixture of alcohols and fatty acids, whereas the ethers split to produce mostly alcohols. Neither of these products will show up in the analyses of the mother compounds and some of the more water soluble products may be lost by diffusion into the overlying water.

Thus by the end of the 150 days experimental period 70-80% of the added Aquamul ethers were still present in the sediment. Ca 10% had been remineralised to CO_2 whereas the remaining 10-20% had most probably been converted to metabolites. Being mostly alcohols, the primary metabolites may have been lost to the watermass or remained present in the sediment as a pool of slowly degrading organic carbon.

The Petrofree ester was completely lost from the sediment by the end of the experiment. However, 53-56% of the added ester carbon had either been lost to the watermass or

remained in the sediment as more refractory phases. The considerable environmental effects of the Petrofree cuttings was most probably driven by rapid decomposition of a pool of easily degradable products, e.g. fatty acids, which had accumulated in the pore waters during the initial rapid (τ = 20 days) hydrolytic cleavage of the Petrofree esters.

The biodegradation of the drilling fluids were accompanied by significant changes in rates of sediment oxygen consumption as well as deviations of pH and E_h in the pore water environment.

Thus, in Petrofree ester treatments, oxygen consumption increased rapidly to a maximum level 5-6 times higher than control chambers. The maximum level was reached ca 30 days after addition and was maintained untill day 80. Large negative deviations of E_h on day 60 as well as the occurrence of black spots and patches of sulphide oxidising *Beggiatoa* mats on the sediment surface showed that hydrogen sulphide had accumulated in the pore water in both Petrofree chambers. The succeeding normalisation of E_h as well as a significant lowering of the pH which most likely resulted from the oxidation of reduced species such as sulphide and divalent iron and manganese ions, showed that the disturbance of the sediment environment had culminated at about day 60.

The maximum loss rate of the Petrofree ester was observed during the 0-30 days period and almost 90% of the ester had disappeared on day 60. However, the oxygen consumption did not reach maximum rates untill day 30 and remained very high untill day 80. This timelag between loss of ester and oxygen consumption showed that the products of the initial hydrolytic cleavage was the primary substrate for the high rates of decomposer activity observed in the Petrofree chambers.

In Aquamul ethers and mineral oil treated chambers, throughout the test, oxygen consumption rates were 2-3 times higher than in the control sediment, and effects on the pore water environment were less pronounced than those observed in the Petrofree treatments. Thus E_h was rarely lowered by more than 50 mV relative to control sediments. Small negative deviations of pH as well as the absence of visual changes on the sediment surface, confirmed that sulphate reduction was a less important process in the degradation of these drilling fluids.

At the deposition sites in the North Sea the choice between the Aquamul ether and the Petrofree ester appears to be the choice between dramatic effects of biodegradation over a smaller area for a shorter period of time and moderate effects over a larger area for a longer period of time.

1 INTRODUCTION

Synthetic drilling fluids for replacement of the mineral oil in mud systems applied in offshore drilling operations are investigated by the oil industry. Aquamul BII is a modification of the previous drilling fluid called Aquamul B. Whereas the Aquamul B drilling fluid consisted of a complex mixture of di-decyl ether isomers, product specifications provided by Anchor Drilling Fluids stated that Aquamul BII was a liquid ether with a purity of 60-100% alkyl ether with a stoichiometric formula corresponding to $C_{20}H_{42}O_2$.

The objectives of the present study was to test the biodegradation and environmental effects of Aquamul BII ethers in drill cuttings deposited on sediments maintained under environmental conditions ressembling as much as possible the conditions at the North Sea seabed, and to compare the behaviour of the Aquamul BII cuttings to other cuttings containing Petrofree® esters[1] and mineral oil, respectively.

2. MATERIAL AND METHODS

2.1 TEST PRINCIPLE

The loss of Aquamul B II ether on cuttings deposited on an experimental seabed was to be compared to the loss of standard mineral oil and Petrofree ester cuttings from replicate seabed systems. This was done by suspending the cuttings in seawater, add the suspensions to the overlying water in benthic chambers and allow the particles to settle

[1]Petrofree is a trade name for a product delivered by Baroid

through the sea water onto the chamber test sediment. The chambers were kept submersed in darkened indoor basins continuously and gently flushed with sea water from 40-60 m depth in the fjord nearby. The total loss of drilling fluids with time was measured by sampling the sediment for drilling fluid analyses at certain time intervals over a total experimental period of 150 days. Biodegradation was calculated from biweekly determination of the sediment oxygen consumption and effects on the pore water environment was assessed from pH and redox potential measurements at various depths in the sediment.

The experimental principle has been developed through several similar projects testing effects of various drilling fluids and different cuttings treatments (Bakke et al, 1989, Bakke and Laake, 1991, Laake et al., 1992, Schaanning and Laake, 1993).

The natural reference of this experiment, should correspond to the conditions found at the seabed surrounding North Sea offshore installations. It is important, however, to realize that it is not possible to make a complete laboratory replicate of any natural system. Therefore, the primary objective of the set-up was to establish identical replicates of experimental systems that contained most of the components present in the natural system.

2.2 SET-UP

The design of the applied benthic chamber and the organisation of the flow system through the eight test chambers is shown in figs. 1 and 2, respectively.

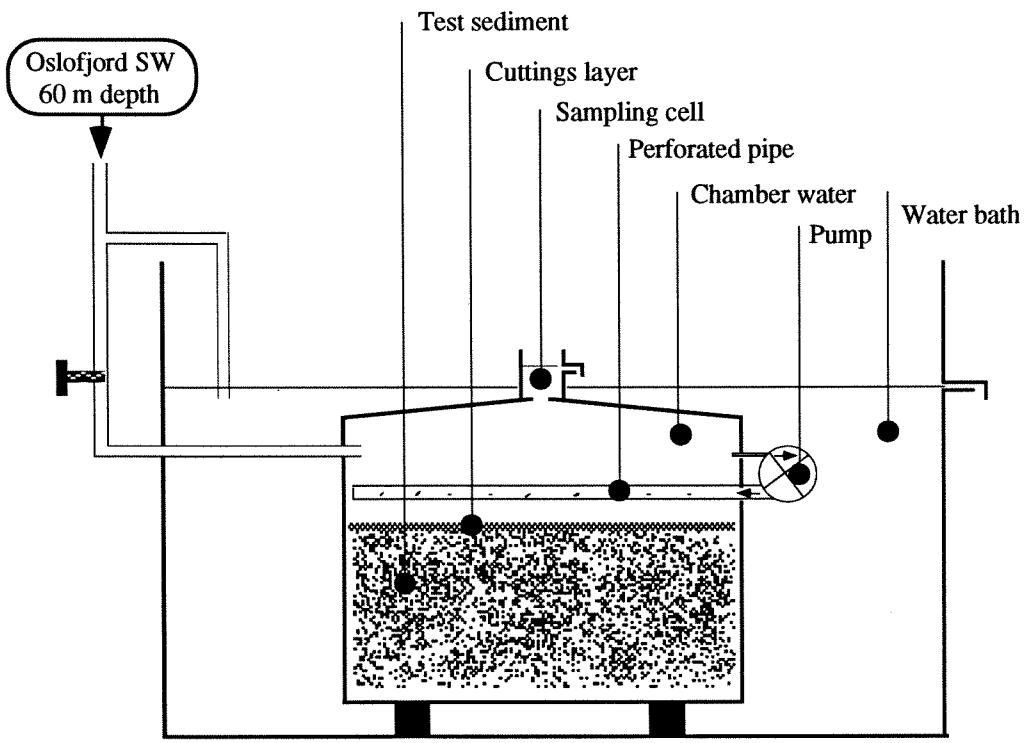

Fig. 1. Schematic drawing of the benthic chamber. Timercontrolled, submersed pumps generated an internal circulation by driving a flow of water through the perforated pipe. To ensure a well mixed chamber water, the pumps were activated for 15 minutes every two hours.

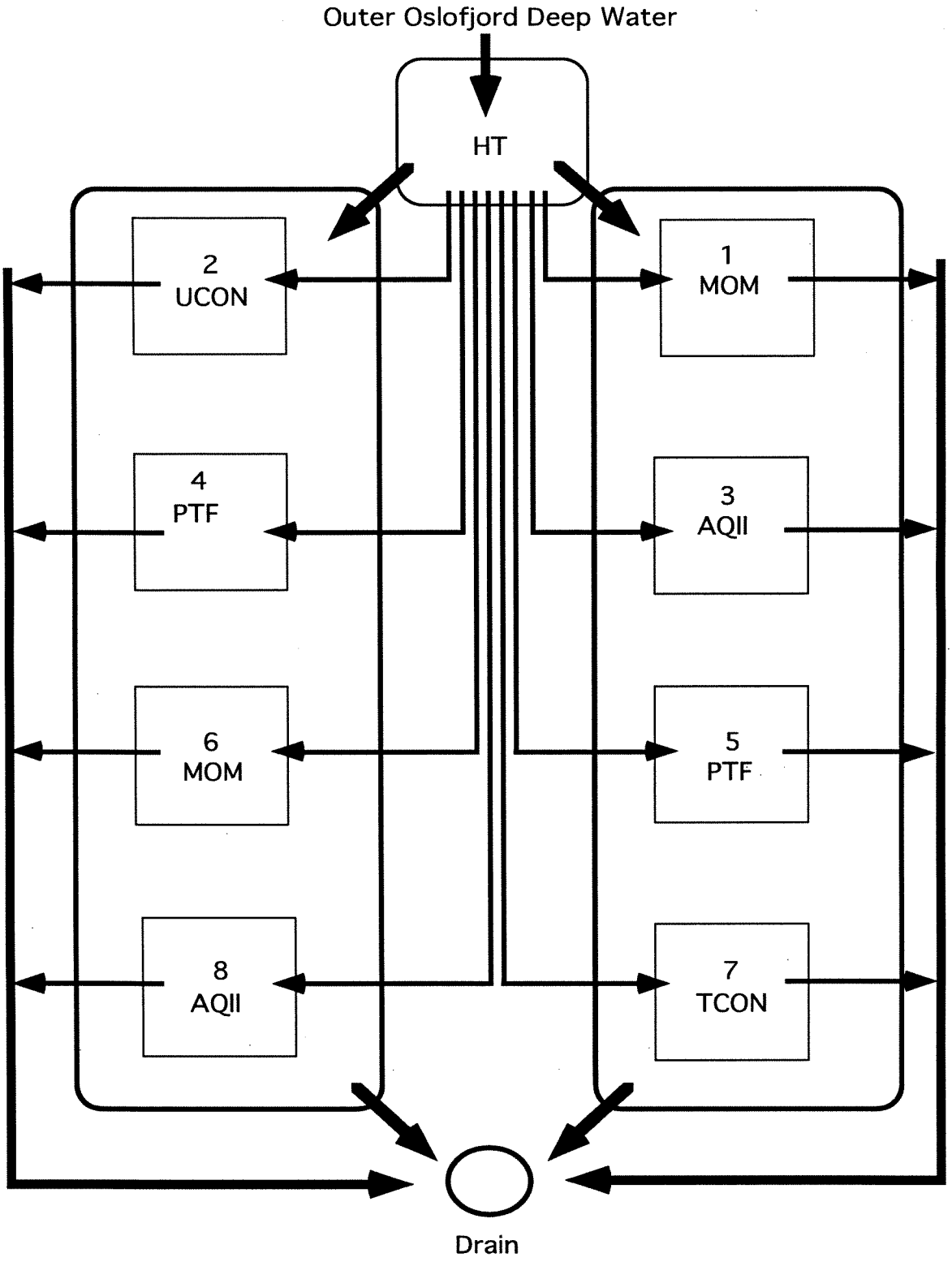

Fig. 2. Schematic drawing of experimental setup and water flow. Fjord water from 40 or 60 m depth were continuously supplied to the header tank (HT). From HT, two peristaltic pumps (not shown) maintained separate flows of water to each chamber. The chambers were kept submersed in two trays which were continuously flushed with overflows from the header tank. Overflow from the trays and boxes were returned to the fjord through the drain.

2.3 TEST ENVIRONMENT

2.3.1 Water quality

The experiment was performed in soft bottom basin 16A at the Solbergstrand Marine Research Station which is situated by the Oslofjord outside the sill at Drøbak. Water for the experiment was continuously supplied from 40 m or 60 m depth. This water exchange with the Skagerrak and the North Sea without restrictions by any sills. As shown in figure 3, the salinity of the source-water ranged between 33 PSU and 35 PSU with occassional spikes down to 31 PSU. The temperature followed the seasonal decline from up to 9°C in the beginning to close to 6°C towards the end of the experiment. Simultaneous shifts to higher temperature and lower salinity during the period Oct-Jan resulted from shifts from the water inlet at 60 m to the inlet at 40 m depth, and vice versa.

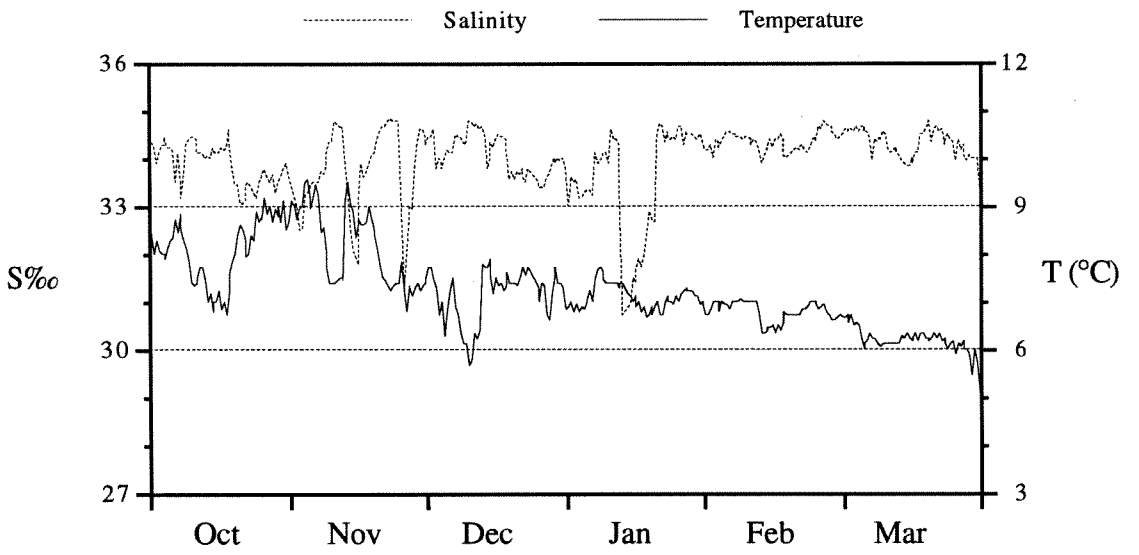

Fig. 3 Salinity and temperature of the source-water during the period 01.10.93-31.03.94. The data was collected by the monitoring programme at the Solbergstrand Research Station (Oen, 1994).

The oxygen concentration of the water entering the chambers varied between 6 and 9 $mg \cdot l^{-1}$. The flow rate through each chamber was adjusted to yield outflow levels of 1-3 $mg \cdot l^{-1}$ less than the water in the header tank. The mean oxygen concentration in the header tank is given in table 1 together with mean outlet oxygen concentration and flow rate through each chamber.

Table 1. Mean oxygen concentration and water flow through chambers during the test period.

	Mean	Std.dev.	n
$[O_2]$ inlet (header tank)	7.43 $mg \cdot l^{-1}$	1.10 $mg \cdot l^{-1}$	41
$[O_2]$ outlet (all chambers)	5.72 $mg \cdot l^{-1}$	1.14 $mg \cdot l^{-1}$	355
Flow (all chambers)	27.7 $ml \cdot min^{-1}$	9.6 $ml \cdot min^{-1}$	355

2.3.2 Sediment quality

The applied sediment was collected 28.09.94 from a non-polluted tidal flat in Elingårdkilen in the Outer Oslofjord. At Solbergstrand, the sediment was rotated for 15 minutes in a concrete mixer and aliquotes of the homogeneous batch was transferred to eight benthic chambers. The chambers (48x48x37cm) were prefilled with a 15cm base layer of nonpolluted sediment. The recently collected sediment was evenly distributed on top of the base layer to constitute a 10 cm layer of the test sediment. The mixing between the two layers was considered to be negligible during test setup and performance. The open chambers were then left submersed in two large trays to equilibrate with seawater from 40m depth.

Table 2. Grain size analyses of the test sediment.

	Grain size interval (mm)	Weight fraction (%)
Granule	2,00 - 4,00	0,295
Very coarse sand	1,00 - 2,00	1,584
Coarse sand	0,50 - 1,00	4,017
Medium sand	0,25 - 0,50	6,975
Fine sand	0,125 - 0,250	21,410
Very fine sand	,063-0,125	43,253
Silt and clay	<,063	22,465
SUM		100,000

The test sediment was analysed for base line parameters such as grain size distribution, water content and organic matter. The grain size distribution (table 2) showed a rather coarse sediment dominated by the fine sand fractions. As shown by the data given in table 3, the test sediment had a low content of organic matter.

Table 3. Water content, loss on ignition, organic nitrogen and carbon in test sediment. Units are % of dry weight. (Analyses performed by NIVA-lab.).

Water	26,3
Loss at 550°C	2,4
TON	<0,10
TOC	0,72

2.4 INITIAL TREATMENT

2.4.1 Test material

The Aquamul II cuttings were sampled from recent drilling operations at the Snorre field in the North Sea. They arrived at NIVA 01.09.93 in carefully sealed plastic bags labelled "Eterfuktet kaks, brønn 34/7-A-9H". The cuttings were kept tightly sealed at 4°C until the set-up of the experiment. According to the result of retort analyses performed at the Snorre field, the ether content of the sample was 3.35 % d.wght. GC analyses performed at the SINTEF-SI laboratory in march -94 on the 34/7-A-9H cuttings sample showed that the cuttings contained a total of 6.06% ethers. The ethers in the sample proved to be a mixture of 60% Aquamul BII ethers and 40% of the previous product Aquamul B.

The Petrofree (reference R-012) and the mineral oil (reference D-82/90) cuttings were taken from cuttings samples left over from previous experiments. The samples originated from offshore drilling operations in the North Sea and arrived at Solbergstrand prior to the test in 1990 (Bakke and Laake, 1991). The chemical analyses performed in 1992 (Laake and Schaanning, 1993) and the preliminary analyses for this test revealed no significant change in total concentration or characteristic

chromatogram patterns during the storage at Solbergstrand. A concentration of THC of 9% has been used for previous calculations on the D-82/90 mineral oil sample. GC-analyses at the SINTEF-SI laboratory in march -94, showed that the concentration of Petrofree esters in the R-012 sample was 11.7 %.

2.4.2 Addition of cuttings

Cuttings were added to the experimental boxes on October 10th.. The water level in the trays was raised to a level 30 cm above the sediments and a column of water above each chamber was enclosed by fitting a frame on top of the open box. Cuttings were mixed with an appropriate volume of seawater in a steel whirl mixer to produce a slurry of suspended cuttings. The slurry was transferred to a glass bottle and added slowly into the water above the respective sediment. Patchy distribution of cuttings on the sediment surface was prevented as much as possible by spreading small aliquots of the slurry over the entire water surface and simultaneously stirring to maintain a turbulent water column. The bottle and mixer was rinsed several times with seawater to obtain quantitative transfer to the chambers. Large particles (hard clay or pebbles) left behind on the bottom of the whirl mixer were discarded. The weight of the discarded material never exceeded 2% of the total weight of the cuttings added.

Thus, the cuttings were added by sedimentation through a 30 cm water column.

2.4.3 Treatments

Two chambers were treated with mineral oil cuttings, two were treated with Petrofree ester cuttings and two were treated with the Aquamul BII cuttings. Another two boxes were used for control. To test for possible effects of capping on oxygen consumption rates and pore water conditions, an aliquot of the non-polluted test sediment was added to one of the control chambers. The amount of cuttings and sediments added to each chamber is given in table 4. The amount of cuttings was chosen to yield concentrations of ca 5000 ppm within the top 0-1cm sediment layer. The amount was calculated using the available information on the cuttings samples and adjusted in accordance with previous experience on loss during treatment procedures.

Table 4. Initial treatment of experimental chambers and recovery of drilling fluids (DF) on the sediment surface on day 0.

Box no	Substance added	Labels	Added		Day 0	Recover
			M_c (g sed.)	C_z (mgDF·cm^{-2})	C_{obs} (mgDF·cm^{-2})	R (%)
2	No add. (Untreated Control)	UCON 2	0	0	-	-
7	Test sediment (Treated Control)	TCON 7	200	0	-	-
1	Mineral Oil Cuttings	MOM 1	160	6.4	2.41	37.7
6	"	MOM 6	160	6.4	2.57	40.1
4	Petrofree Ester Cuttings	PTF 4	185	9.4	4.16	44.3
5	"	PTF 5	185	9.4	4.11	43.7
3	Aquamul BII Ether Cuttings	AQII 3	410	6.7	8.89	132.7
8	"	AQII 8	410	6.7	9.00	134.3

2.4.4 Initial effects

After addition the boxes and frames were left undisturbed to allow fine fractions to settle out of the water column. 20 hours later, some turbidity was still present in the watercolumn. An oxygen electrode showed the presence of 6.6-8.1 $mgO_2 \cdot l^{-1}$ in the water just above the sediment surface. Some of the cuttings had settled on the walls of the boxes and frames. This material was gently wiped off into the watercolumn and allowed to settle out for another day.

44 hours after addition of cuttings, oxygen concentrations at the sediment surface were still as high as 6.6-7.2 $mgO_2 \cdot l^{-1}$. The slight turbidity from the day before had gone and the cuttings particles appeared to have settled out almost completely. The added material was seen present in a distinct layer on top of the test sediments. The thicknes of the layers was estimated to 1-3mm, and the colours varied from grey control sediment via lighter grey-yellow in the Petrofree and mineral oil treatments to a characterisic red colour of the Aquamul cuttings.

Animal tracks in the fresh layers showed that individuals of the sediment infauna had been active on the sediment surface during the period of addition and sedimentation. Tracks were observed on all treated sediments control included, whereas no tracks were seen on the untreated control sediment. Thus, the treatment appeared to cause some

disturbance of the benthic infauna. However, no dead animals were observed on the sediment surface and the fact that the addition of control sediment produced similar effects gave no evidence for relating this behaviour to toxicity of components present in the cuttings. Neither did the concentration of oxygen in the bottom water drop to critical levels. Therefore, the effect is more likely to have been a physical disturbance caused by clogging of irrigation tubes and burrows.

Before sealing the boxes with tight fitting lids, and initiation of the water circulation system (fig.2), zero sampling for determination of drilling fluid concentrations in the sediment and pH and redox potentials in the pore water were performed.

2.4.5 Recovery of added drilling fluids

The added amounts of cuttings (M_C) and the recovery (R) found on the sediment surface during the day zero sampling is given in table 4. If the concentration of the respective drilling fluids in the cuttings sample is C_C and the box area A=0.23m^2, the calculated concentration on the sediment surface C_Z

$$C_Z = M_C \cdot C_C / A$$

and the recovery (R) on the sediment surface can be calculated from

$$R = C_{obs} \cdot 100 / Cz$$

Table 4 showed a range of recoveries between 38 and 134 %. Recoveries less than 100% should be expected to result from adherence of drilling fluids to the steel mixer, slurry container, walls of chamber and frame or from loss to the water as dissolved drilling fluids or attached to floating particles. In a previous test, recoveries of 25-81% was found for sediments treated with Petrofree and the mineral oil cuttings.

Recoveries exceeding 100% was found in both boxes treated with the Aquamul ethers. Recoveries of more than 100% was also found in a previous test of a polyalfaolefin based drill fuid. Recoveries of more than 100% are absurd and indicate the presence of errors in the determination of Aquamul ether concentration in cuttings or sediments. Possible sources of error involve uneven distribution of drilling fluid in the cuttings samples analysed or added, non-linear dilution of the very high concentration of drilling fluids in the cuttings and variable drilling fluid behaviour due to variations in sample matrix between sediments and cuttings.

Thus, a mass-balance mismatch of about 50% should not be considered a big suprise. The test was never intended to describe the potential for loss of drilling fluids between discharge point and seabed. The calculation of the recovery was undertaken primarily to test the validity of assumptions inherent in test setup and analytical procedures. Unfortunately, it has revealed a problem with regard to predicting a given sediment concentration of certain types of drilling fluids. The problem should not, however, have any consequences as to the validity of the assessment of the loss of drilling fluids from the sediment relative to concentrations observed on day zero. Thus, the test can only adress differences in the behaviour of drilling fluids after seabed deposition.

2.5 SAMPLING, ANALYSES AND ERROR ESTIMATES

The time table of the sampling programme is shown in table 5.

Table 5. Time table of sampling programme. The table shows total number of analyses performed on samples collected at specified dates 0-5 months after the sedimentation of cuttings.

Date	26.10	29.10	29.11	28.12.93	31.01.94	24.02	23.03
real time	0	3	33	63	96	120	146
Activity \ nom. day		0	30	60	90	120	150
Mud added	✓						
DF-analyses:							
AQII-ether		6	2	2	2	2	6
AQI-ether[1]		6	2	2	2	2	6
PTF-ester		6	2	2	2	2	6
THC		6	2	2	2	2	6
Other analyses:							
pH (9/box)		72	72	72	72	72	72
E_h (9/box)		72	72	72	72	72	72
SOC (1/box)		|---------- twice a week ----------|					
Water temp. (°C)	|---------- continuously ----------|						
" salinity (S‰)	|---------- continuously ----------|						

[1]Analyses performed on same sample extract as AQII-ether.

2.5.1 Oxygen Consumption Measurements

Oxygen consumption within each chamber was determined by measuring the rate of the flow of water through each chamber as well as the drop in concentration of oxygen between the common inlet (HT) and each separate outlet.

The sediment oxygen consumption SOC, was calculated from the equation:

(eq. 2.1) $$SOC = (C_i - C_o) \cdot F/A$$

in which

C_i is the concentration of oxygen in the water entering the tray
C_o is the concentration of oxygen in the water leaving the tray
F is the flow rate of the water
A is the area of the tray

Thus, the contribution to SOC from oxygen consumed by microorganisms present in the water or attached to tubes and chamber walls were assumed to be small compared to the oxygen consumption of the sediment. Furthermore, if the magnitude of the blank respiration is similar in control and treated chambers, this error is eliminated from biodegradation assessments based on the difference between treated and control sediment (ΔSOC).

2.5.2 Electrode measurements

Electrode measurements were done *in situ* by inserting electrodes directly into the submersed sediments at three different locations within each tray. pH was measured using an Orion Ross 81-04 glass combination electrode. Redox potentials were determined on a standard Radiometer P101 platinum electrode against the internal reference of the pH combination electrode. The electrodes were inserted to successive positions 5, 15 and 25 mm below the sediment-water interface. The pH and redoxpotential were recorded as soon as the pH was stable.

Before the first sampling date, a two point calibration of the pH were performed using dilute IUPAC buffers of pH 7 and 4. On this scale, the pH of the fjord water supplied to the chambers was found to be 8.05. pH-variations at 40-60m depth is known to be small. Thus, throughout the experiment, pH was determined using the supply water as a substandard with an assumed constant pH of 8.05. The pH of the supply water was determined before and after the measurements in each chamber. Some variation in the pH of the fjord water may have occurred during the experiment, but the corresponding error in the absolute pH measured in the pore water was probably less than 0.2 pH-units. All calibrations and measurements were done at the experiment temperature of 6-10°C.

The redox circuit was checked in a ZoBell Fe(II)-Fe(III) redox-buffer solution with a redoxpotential of 430 mV at 20°C. The E_h of the buffer solution decrease with decreasing temperature. At 10°C the half-cell potential of the Orion Ross 81-04 is 431mV (Orion product specifications). The E_h of the samples were obtained by adding 431mV to the rest-potential recorded on the Pt-electrode. Thus, as recommended by ZoBell, 1946, the electrode was checked, but not calibrated with the redox buffer.

2.5.3 Reproducibility of pH and E_h measurements

During the experiment, the pH was measured at three depths in three locations in eight chambers at six sampling occasions. Thus a total of 432 single determinations of pH were performed. The standard deviation calculated for the six measurements taken at each depth on each occasion and for each treatment will express the magnitude of the random variations or reproducibility of the pH measurements. As shown in table 6, the mean pH of the 72 sets of data ranged from 6.91 to 8.46 and the corresponding standard deviations ranged from 0.02 to 0.20 pH units. If the reproducibility of the pH measurements is taken to be the mean value of the standard deviations, the reproducibility was found to be .09 pH-units (n=72) or 5.8% of the range of the pH variations.

Similarly, the range of measured redox potentials ranged from -171 mV to +203 mV (table 6). The corresponding standard deviations ranged between 1 mV and 93 mV with an average standard deviation of 33 mV (n=72). The higher range of values were recorded before a stable potential was obtained. Values of about 400 mV have frequently been obtained in similar environments when allowing sufficient response times. Because, however, the major objective for using this test parameter was to assess the deviations from the control sediment, the reproducibility of the measurements,

rather than their accuracy, determines how good the method is to assess effects of a certain treatment. The reproducibility of the E_h measurements, as given by the mean standard deviation, was 33 mV. This corresponded to 8.8% of the range of the E_h variations.

In other words, effects of the treatments which imply deviations from control sediments of E_h larger than 33 mV and pH larger than 0.09, are likely to be revealed by this test.

Table 6. Range of 24 mean values and standard deviations of the 6 parallel electrode measurements at each depth level.

	Mean values			Standard deviations		
Sample depth (mm)	5	15	25	5	15	25
Maximum pH and std.dev. (pH-units)	8.46	8.24	7.90	.20	.17	.16
Minimum pH and std.dev. (pH-units)	7.40	7.12	6.91	.02	.04	.04
Maximum E_h and std.dev. (mV)	203	167	149	93	55	81
Minimum E_h and std.dev. (mV)	-117	-163	-171	6	1	8

2.5.4 Collection of sediment samples

13 mm (ID) polyethylen cut-off syringe cores were inserted to a sediment depth of 3-5 cm. By placing the thumb over the open end, the sediment trapped inside the core could be withdrawn with a minimum of disturbance. Erosion at the edges of the cavity left in the sediment was prevented by immediate reinjection of control sediment from an identical syringe core. At the laboratory bench, the syringe piston was inserted to push the top layer into a slicing cell. Thus, a precise segment of the surface layer was cut off using a thin sheet of PVC and transferred to a preweighed glass container. Five cores from randomly chosen locations (fig. *f*2) were transferred to each container to make up one sample for chemical analyses. The total weight of the sample was determined and a subsample for measuring dry weight was collected before sealing the sample container with a polyethylene cap. Less than four hours after removal of the core sample from the trays, the samples were put aside for storage at -15°C until analyses at the SINTEF-SI laboratory.

The sample positions were determined by dividing the chamber area in a grid of 100 4x4 cm squares (fig. 4). Each grid was identified by a coordinate number from 00 to 99 and fifty grids were chosen for sampling using the random number generator of a

computer spreadsheet. Thus the first number determined the sampling position for core no 1, sample 1, day zero, the second number determined the position of core no 2, sample 1, day zero etc. In cases of duplicate number generation a free neighbouring grid was chosen. All chambers were sampled equally.

The coordinates were marked on the edges of each chamber, and the cores were drawn from the center of each grid by positioning a wire cross over the chamber area. To avoid edge bias, the grid area was deliberately made smaller than the chamber area. Thus no cores were drawn from a location less than 6cm away from the edge of the sediment surface.

In ch. 2.5.5, table 7, random errors in drilling fluid analyses obtained using this sampling strategy is compared to previous results using one large core.

2.5.5 Drilling fluid analyses

Analytical procedures for drilling fluid analyses are given in Appendix 1.

Briefly, the work-up of the mineral oil samples were performed following a UNESCO standard procedure based on saponification in methanolic KOH and extraction in dichloromethane. Polar compounds were removed by chromatographing on silica columns. The work-up procedures for Petrofree esters and Aquamul ethers were based on Soxhlet extractions using successively methanol and dichloromethane.

All sediment extracts were analysed on a gas chromatograph using flame ionization detector. Total hydrocarbon levels in the mineral oil sediment extracts were determined against a mineral oil standard. Petrofree esters and Aquamul ethers were quantitated by addition of known amounts of internal standards to each sample.

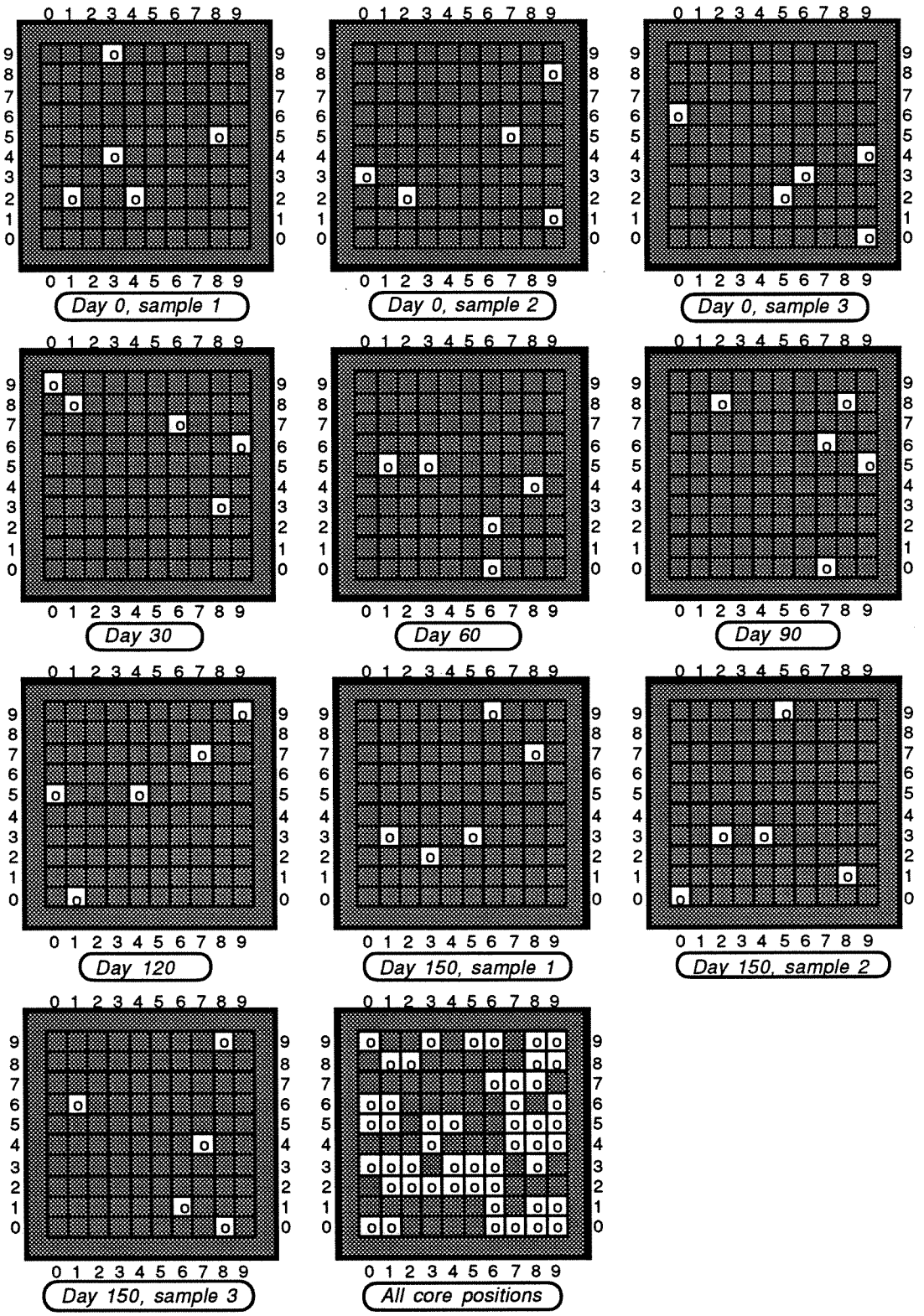

Fig. 4. Grid system and sampling locations chosen by random number generation

2.5.6 Units and errors in drilling fluid analyses

Large random errors in drilling fluid analyses has been a major problem in the interpretation of previous test results. Large variations in concentrations in simultaneous samples, have perturbated the significance of time trends. Such variations may result from a number of sources such as patchy distribution on the sediment surface, core sampling techniques, sample handling and storage, drilling fluid extraction procedures and GC-analyses. It is a frequent experience that the errors in well established laboratory procedures are small compared to natural variations resulting from uneven initial sedimentation of cuttings as well as an animal driven redistribution during the course of the experiment.

During previous studies, samples were drawn using larger cores (ID≈4 cm) and each core sample was analysed separately. In the present experiment, the large core sampling on one random location was replaced by five small cores sampling on five random locations. Thus patchy distribution might become less of a problem and random errors originating in core sampling and sectioning should be averaged out.

Because of the fact that the cuttings were added to form a <2mm thin layer on top of the sediment, accurate sectioning of the core sample is particularly important. The sediment surface is neither perfectly flat nor horizontal. Thus, accurate sectioning of the surface layer of the sediment is more difficult to obtain the larger the diameter is of the core applied.

Another way around this problem is to relate the content of drilling fluid to sediment area rather than to sediment weight. The concentration measured in mg drilling fluid per g dry sediment will be crucially dependent on the weight of the sampled core segment. A variable length of the core segment or a bumpy or tilting sediment surface will imply variable dilution of the cuttings in clean sediment. Thus for intercomparison of drilling fluid concentrations, it is crucial that not only a standard length of core segment is sampled for analyses but also that the sectioning technique is very accurate.

In order to relate the content of drilling fluids to the sampled area, the length of the core segment must exceed the thickness of the cuttings layer, and the total weight of the sampled segment (M_S) must be determined in addition to the water content (W) and drilling fluid concentration per g dry sediment (C_Z). The concentration per sediment area (C_A) can be calculated from:

(eq. 2.2) $C_A = C_Z \cdot M_S \cdot (100-W)/100 \cdot A \cdot n$

in which A is the core area and n the number of cores pooled in each sample. In the present study, M_S and W was determined and C_A calculated from the result of the analyses in Appendix 2, using eq...

The random errors for the analyses of Petrofree esters and mineral oil THC obtained from a previous experiment (Schaanning and Laake, 1993) are reproduced in table 7 along with the relative standard deviation of C_Z and C_A for all data obtained on day zero and day 150 of the present study. The comparison shows that the change of sampling strategy has led to a major reduction of random errors in drilling fluid analyses. Wether the major improvement resulted from better representation of a patchy distribution or the reduction of errors due to inaccurate core sectioning cannot be assessed from the data given in table 7. The fact that even when averaged on five sectioning operations a reduction of the relative error from 13.9% to 11.2% indicates that accurate sectioning of the sediment surface is a major problem which may be eliminated by relating the drilling fluid content to surface area rather than to sediment weight.

Table 7. Relative standard deviation of C_Z and C_A. Each number result from the analyses of 4-6 samples. During the previous study each sample was drawn separately in one large core. During the present study, each sample was pooled from six cores taken at random locations.

	Previous study	This study	
	C_Z (mg·kg^{-1})	C_Z (mg·kg^{-1})	C_A (mg·cm^{-2})
	Relative standard deviation (%)		
MOM-THC, initial	19.9	16.8	9.4
MOM-THC, final	12.2	15.4	14.8
PTF-Esters, initial	31.0	9.4	8.3
PTF-Esters, final	15.4	12.9	10.3
AQII-Ether, initial		15.8	14.6
AQII-Ether, final		13.3	9.6
Mean	19.6	13.9	11.2

3 RESULTS AND DISCUSSION

3.1 DIRECT POTENTIOMETRIC MEASUREMENTS

pH and E_h are superior chemical parameters, primarily controlled by mineral acid-base and reduction-oxidation equilibria in the sediment. Cuttings may contain components that react spontaneously to displace such equilibria and alter the potentials recorded during a short time following the treatment. Thus, in previous tests (Ref.), the pH has been observed to show an immediate increase after the addition of certain types of cuttings containing carbonate or hydroxide salts such as $Ca(OH)_2$ and $CaCO_3$. Corresponding, non-biological effects on E_h have not been observed. Biological processes triggered by the introduction of any degradable organic matter, will increase the concentration of decomposition products in the pore water. This is known to produce a decrease of pH and E_h and will occur at a timescale of hours and weeks. Because of the low levels of incoming light energy, fixation of CO_2 is not believed to contribute significantly to pore water equilibria neither in this experiment nor at the deposition sites in the North Sea.

All results of the electrode measurements are given in table A1.1. Fig. 5 shows the variation with time of the difference between the various treatments and the untreated control sediment at each depth. Table 8 shows the statistical significance of the difference between the pH and E_h in each of the cuttings treatments and both control chambers.

3.1.1 pH

Considering the pH as an environmental factor, the magnitude of the pH-deviations was very moderate. All pH-values recorded throughout this study were well within agreed environmental quality criteria (Wolff et al, 1988). Thus, the pH variations would not have any significant biological implications. The pH variations may however, elucidate the localisation, timing and intensity of microbial processes in the sediment.

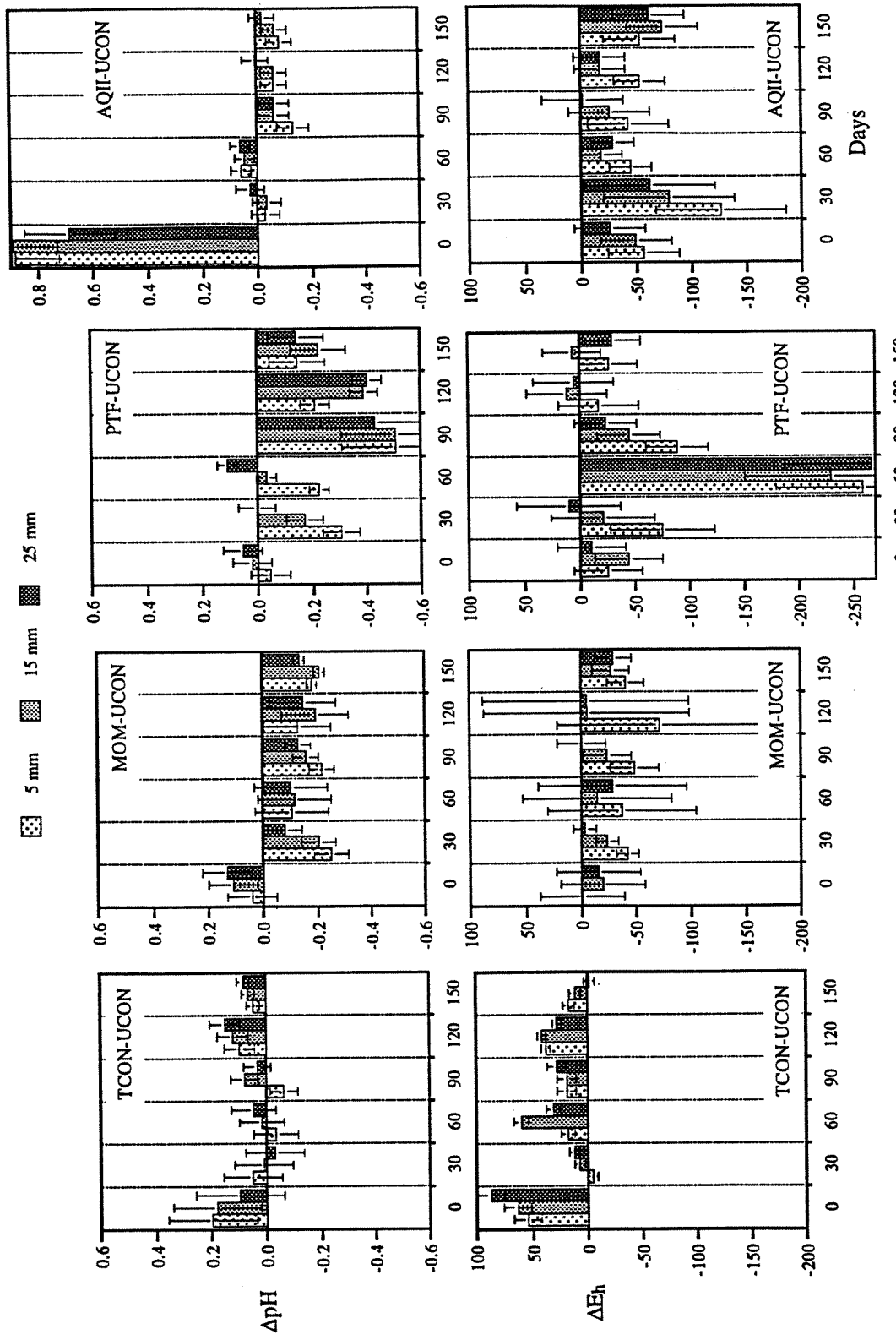

Fig.5. Deviations of pH and redox potentials in treated control sediment (TCON) and sediments treated with mineral oil cuttings (MOM), Petrofree ester cuttings (PTF) and Aquamul BII ether cuttings (AQII) from untreated control sediment (UCON). Vertical bars represent ±1 standard deviation of six parallel measurements in two treated chambers (n=6).

Table 8. Observed pH and Eh in control sediments, as well as magnitudes and statistical significance of deviations in treated sediments. The variance of the data was analysed using the statistic software package StatView®II. - means not significant at 95% confidence level. + means significant difference according to Fisher PLSD. ++ means significant difference according to Fisher PLSD and Scheffe`s F-test.

		pH							Eh						
Day	Depth (mm)	con	Δmom	Δptf	Δaqii	Δmom	Δptf	Δaqii	con	Δmom	Δptf	Δaqii	Δmom	Δptf	Δaqii
			pH-units			significant at 95%				(mV)			significant at 95%		
zero	5	7.68	-0.06	-0.14	0.79	-	-	++	177	-28	-52	-83	-	+	++
	15	7.44	0.02	-0.07	0.80	-	-	++	133	-52	-76	-81	+	++	++
	25	7.26	0.09	0.01	0.64	-	-	++	90	-59	-54	-69	+	+	+
30	5	7.91	-0.28	-0.33	-0.06	++	++	-	136	-40	-73	-124	-	++	++
	15	7.62	-0.21	-0.18	-0.04	++	+	-	94	-27	-24	-83	-	-	++
	25	7.36	-0.07	0.01	0.04	-	-	-	61	-9	5	-68	-	-	++
60	5	7.76	-0.08	-0.20	0.08	-	++	-	150	-46	-267	-53	-	++	-
	15	7.52	-0.12	-0.04	0.04	+	-	-	132	-72	-300	-58	+	++	+
	25	7.33	-0.12	0.09	0.04	++	+	-	106	-80	-281	-66	+	++	-
90	5	7.88	-0.18	-0.48	-0.10	+	++	-	179	-58	-98	-53	++	++	++
	15	7.66	-0.19	-0.54	-0.09	++	++	-	131	-33	-54	-35	++	++	++
	25	7.48	-0.14	-0.44	-0.07	+	++	-	103	-15	-38	-16	-	++	-
120	5	7.79	-0.18	-0.26	-0.11	++	++	+	202	-90	-36	-72	+	-	+
	15	7.58	-0.26	-0.46	-0.13	++	++	-	133	-27	-9	-38	-	-	-
	25	7.39	-0.22	-0.48	-0.07	+	++	-	115	-19	-9	-31	-	-	-
150	5	7.84	-0.20	-0.17	-0.11	++	++	+	203	-49	-37	-62	++	++	++
	15	7.67	-0.24	-0.26	-0.10	++	++	-	166	-33	-1	-80	-	-	++
	25	7.50	-0.18	-0.19	-0.07	+	+	-	149	-28	-26	-60	-	-	++

Thus, as shown in the left hand diagram of fig.5 (TCON-UCON), the pH was observed to increase by up to 0.2 pH-units as a result of the addition of thin layer of control sediment. The magnitude of this effect decreased with depth. 30 days after the treatment the difference between the two control chambers was negligible. The ΔpH remained negligible at days 60 and 90. At day 120 a slight increase of the treated relative to the untreated control had occurred, but at day 150 the mean difference was again less than the experiment reproducibility of ±0.09 (ch. 2).

If the cuttings were indifferent from control sediment, the response should have been similar to the TCON response. Both PTF and MOM showed a slight initial increase at 25 mm depth, which indeed was similar to the TCON effect. However, at the sediment surface, even though the pH was not significantly different from the pH in the untreated

control, it was less than in the treated control sediment. At day 30, fig.5 and table 8 shows a significant surface lowering of the pH relative to any of the control sediments. Thus, the lowering of the pH which later on became more significant was observed to begin developing at the sediment surface at day zero.

The largest negative pH deviations was observed in the Petrofree ester treatments at day 90. This decrease succeeded the major drop of the redox potential observed at day 60. In the Aquamul treatments, the major positive pH anomaly observed at day zero was probably the result of rapid dissolution of carbonate or hydroxide salts present in the mud. 30 days after the treatment, the pH had normalised and significant deviations from the control sediment was rarely observed (table 8). Because both oxygen consumption and redox potentials did suggest a stimulated microbial activity, the zero effect on pH may rather than no effect, represent a net zero resulting from a positive deviation from the salts and a negative deviation from biodegradation.

3.1.2 E_h

If oxygenated seawater with a higher pH and E_h is trapped during sedimentation of the new top layer, the pH and E_h of the top layer should increase as a result of the addition of control sediment. Both pH and E_h showed initial positive deviations in the treated control sediment (fig.5). On day 30, however, the difference of the E_h between the two control chambers was negligible at all depths. Throughout the remaining experiment, the difference rarely exceeded the test reproducibility of ±33mV (ch.2).

As shown in table 8, the mean E_h in the control sediments ranged from +61mV to +203mV. Highly negative redox potentials were observed in the PTF treatments on day 60. Then, 14 of 18 recordings in the two PTF chambers ranged between -148 mV and -200 mV. These negative potentials are characteristic for sulphidic environments.

Apart from the sulphide event in the Petrofree chambers, neither black spots from sulphide precipitations nor any smell of H_2S-gas was detected at any time during the present experiment. As shown in table 8 the E_h in most samples ranged 10-100 mV below control sediments and no clear trends could be observed neither between treatments nor with time. Apart from the PTF-event, the largest negative deviations were observed in the Aquamul ether treatments at day 0, 30 and 150.

Iron and manganese redox couples may be important controls of the redox potentials in the 0-100mV E_h-range. It can be shown that lower pH, oxygen activity and higher

sulphide activity should displace the Fe^{2+}/Fe^{3+} activity ratio towards higher activity of Fe^{2+}, which again might imply a moderate lowering of the E_h as observed in most chambers throughout the study. However, because of the initial rise of pH in AQII, the simultaneous drop of the E_h was not consistent with manganese or iron redox controls.

Thermodynamic interpretations of observed potentials are generally not recommended. Numerous redox couples may be present to contribute to the recorded potential, and the different behaviour of the Aquamul cuttings may result from differences in the mineralogic composition of the cuttings as well as components added with the mud.

3.1.4 Effects of biodegradation on pH and E_h

The stoichiometry of the drilling fluids can be modelled by compounds intermediate between a saturated hydrocarbon (C_nH_{n+2}) and a carbohydrate ($C_n(H_2O)_n$). If degradation is driven primarily by oxygen respiration the overall process can be written:

(eq.3.1) $$C_nH_{n+2} + 2nO_2 = nHCO_3^- + nH_2O + nH^+$$

or

(eq.3.2) $$C_n(H_2O)_n + nO_2 = nHCO_3^- + nH_2O + nH^+$$

Within the actual range of pH of 7-8, the bicarbonate ions will not buffer the pH reduction predicted by right-hand reactions in eqs 3.1 and 3.2.

If degradation is driven primarily by sulphate reduction, the overall process can be written:

(eq.3.3) $$C_nH_{n+2} + nSO_4^{2-} = nHCO_3^- + nH_2O + nHS^-$$

or

(eq.3.4) $$C_n(H_2O)_n + n/2SO_4^{2-} = nHCO_3^- + n/2HS^- + n/2H^+$$

Within the actual range of pH of 7-8, hydrogen sulphide will be present primarily as HS^- (bisulfide ions). If pH approach 7.0 bisulphide ions will act as a buffer by protonation to H_2S molecules. Thus with the carbohydrate type of organic carbon,

sulphate reduction will tend to lower the pH to a value of about 7.0, which in effect represent the lower boundary of pH in natural sediments dominated by sulphate reduction (Ben-Yakov, 1978). Equation 3.3 shows, however, that sulphate reduction of saturated hydrocarbons should not yield any pH-reduction at all.

The production of hydrogen sulphide is known to trigger a characteristic redox-cycling of iron and manganese at the sediment-water interface. This cycling may have effects on the pH which is superimposed on the effects of the degradation processes. The cycling may involve dissolution by reduction of oxides:

(eq.3.5) $FeOOH + 1/2HS^- + 5/2H^+ = Fe^{2+} + 1/2S_0 + 2H_2O$,

and

(eq.3.6) $MnO_2 + HS^- + 3H^+ = Mn^{2+} + 1/2S_0 + 2H_2$,

upwards diffusion of the divalent ions and precipitation by reoxidation in the oxic environment at the sediment surface by

(eq. 3.7) $Fe^{2+} + 1/4O_2 + 3/2H_2O = FeOOH + 2H^+$.

and possibly

(eq. 3.8) $Mn^{2+} + 1/2O_2 + 3H_2O = Mn(OH)_4 + 2H^+$.

If the concentrations of Fe^{2+} and HS^--ions increase to exceed to solubility product of ferrous sulphide $K_{FeS} = \{Fe^{2+}\}\{HS^-\}$, black FeS precipitates:

(eq.3.9) $Fe^{2+} + HS^- = FeS + H^+$.

Because of the much higher solubility of MnS and the slow kinetics of manganese oxidation, Mn^{2+} is more likely to accumulate in the pore water and diffuse towards the sediment surface and even escape into the chamber water.

The reactions described in eqs.3.5-3.9 may yield quantitatively significant contributions to pH-anomalies. In addition bisulphide ions may diffuse towards the sediment surface at which it may react with oxygen to produce elemental sulfur as a metastable intermediate before complete reoxidation to sulphate:

(eq.3.10) $HS^- + 2O_2 = SO_4^{2-} + H^+$.

If the Petrofree esters are more available substrates to sulphate reducing organisms than mineral oil and Aquamul ether, the major processes affecting pH and redox potentials at 25 mm depth may be described by right-hand reactions of the stoichiometric relationships:

(eq.3.3) $C_nH_{n+2} + nSO_4^{2-} = nHCO_3^- + nH_2O + nHS^-$

(eq.3.5) $FeOOH + 1/2HS^- + 5/2H^+ = Fe^{2+} + 1/2S_0 + 2H_2O$

(eq.3.6) $MnO_2 + HS^- + 3H^+ = Mn^{2+} + 1/2S_0 + 2H_2O$

It appears that the acid consumed during iron and manganese reduction might contribute to an increase of the pH. As shown in fig.5, during the first 60 days, the pH had a more positive trend at 15 and 25mm depth in the Petrofree as compared to the mineral oil treatments. This trend appeared to culminate with the significant positive deviation at 25 mm depth on day 60 (table 8).

If sulphate reduction produce bisulphide ions faster than they are consumed by reduction of the metal oxides, the concentration of bisulphide may increase to take over the control of the potential on the Pt-electrode. If so, the E_h should drop to low values (<-100 mV). If consumption of bisulphide is as fast as production, concentration of sulphide is kept low and the potential on the Pt-electrode may be controlled by Fe^{2+}/Fe^{3+} and Mn^{2+}/Mn^{4+} redox couples. An E_h of about 0-50mV is predicted by the most common iron and manganese equlibria. Thus, increased activities of Fe^{2+} and Mn^{2+} might explain the moderate lowering of the E_h observed in all treatments throughout the experiment, but the large drop observed in the Petrofree treatments on day 60 indicated that sulphate reduction had proceeded to a stage at which sulphide accumulated in the pore water. Such a sulphide event was clearly confirmed by the formation of black spots of FeS and white precipitates of elemental sulfur on the sediment surface.

The reduced ions (Fe^{2+}, Mn^{2+}, HS^-) may be transported by diffusion towards the sediment surface at which oxidation may occur according to eqs. 3.7, 3.8 and 3.10. In addition the solubility product of FeS may have been exceeded so that precipitation occurred according to eq. 3.9. All of these reactions will tend to lower the pH as was indeed observed to have occurred in the Petrofree treatments at days 90 and 120 (table

8, fig.5). Thus a normalisation of E_h values resulting from consumption of the pool of hydrogen sulphide established on day 60, was consistent with the pronounced drop of pH observed in the Petrofree treatments on days 90 and 120.

In the mineral oil and Aquamul ether treatments, slow sulphate reduction may have caused a slight reduction of redox potentials by accumulation of reduced iron and manganese. If sulphate reduction was slow at depth in the sediment, a more dominating impact of oxygen respiration (eq.3.1) may be responsible for the negative deviation of pH in the mineral oil treatments. In the Aquamul treatments the microbial processes were probably similar to those in the mineral oil treatments, but the mineral buffers responsible for the initial high pH in the Aquamul cuttings, may have set a higher level of pH throughout the experiment.

Thus, if the variations of redox potentials and pH were controlled by the bacterial degradation of hydrocarbons according to the models proposed above, the observed deviations from control sediments showed that the Petrofree esters were more available to decomposition by sulphate reducing bacteria than mineral oil and Aquamul ethers. Sulphate reduction is a frequently occurring natural process in many coastal sediments. Because, however, of the toxicity of the hydrogen sulphide produced, a stimulated sulphate reduction may produce dramatic structural changes of the composition of the benthic community.

3.2 CHEMICAL ANALYSES

All results of the gas chromatographic analyses of Aquamul ethers, Petrofree esters and mineral oil hydrocarbons (THC) are given in Appendix 2. Recalculated values to total content below each cm^2 sediment surface (see ch.2.5.6) are given in Appendix 1, table A2, and in table 9 and fig.6 below. Over the entire experimental period declining concentrations were found for all drilling fluids.

Table 9. Initial and final concentration of drilling fluids (± one standard deviation) for the test period. (Concentrations in $mg \cdot cm^{-2}$.)

	Petrofree	Mineral oil	Aquamul B	Aquamul BII
Day 0	4.130 ± 0.340	2.49 ± 0.34	2.58 ± 0.47	8.95 ± 1.31
Day 150	0.034 ± 0.003	1.99 ± 0.29	2.20 ± 0.41	7.71 ± 0.74
Loss	4.096	0.50	0.38	1.24
Relative loss	99.2%	20.1%	14.7%	13.8%

Table 9 show that whereas 99.2% of the Petrofree esters had disappeared from the sediment during the 150 days experimental period, only 13.8-20.1% of the mineral oil and Aquamul ethers were lost.

First order kinetics are frequently used to describe chemical reactions only dependent on the concentration of the reactant. The general form of a first order reaction is:

(eq.3.11) $C = C_0 \cdot 10^{-kt}$

in which:

C = concentration
C_0 = initial concentration
t = time
k = rate constant

The regression lines plotted in fig. 6, show the best fit of the data to first order reaction models. The significance of each trend is given by the correlation coefficient r. If $r \geq 0.44$ (≥ 0.47 for MOM) the correlation between time and sediment concentration is positive at a 95% significance level. The correlation coefficients varied from 0.482 for the Aquamul B ether to 0.994 for the Petrofree ester. Thus, trend analyses using all data yielded significant loss at the 95% significance level for all drilling fluids tested.

From eq. 3.11, it can be shown that if the half-life τ is the time at which $C=C_0/2$, $\tau = 0.302/k$. As shown in fig. 6, half-lifes calculated were 20.3 days for the Petrofree ester, 399 days for mineral oil THC, 392 days for Aqumual B ether and 536 days for the BII ether. As shown by the rather low correlation coefficients, calculated half-lives exceeding the experimental period were rather uncertain. Thus, the long time calculated for the Aquamul BII ether as compared to mineral oil and Aquamul B, may be the result of a higher initial concentration.

Note that, apart from the Petrofree data, correlation coefficients calculated for linear models were not much different from those calculated for the exponential model. Thus the results gave no evidence as to which model gives the best description of the loss with time of mineral oil THC or Aquamul ethers. The half-lives calculated from the curve equations do however depend on the model chosen. The linear models yielded slightly shorter half-lives.

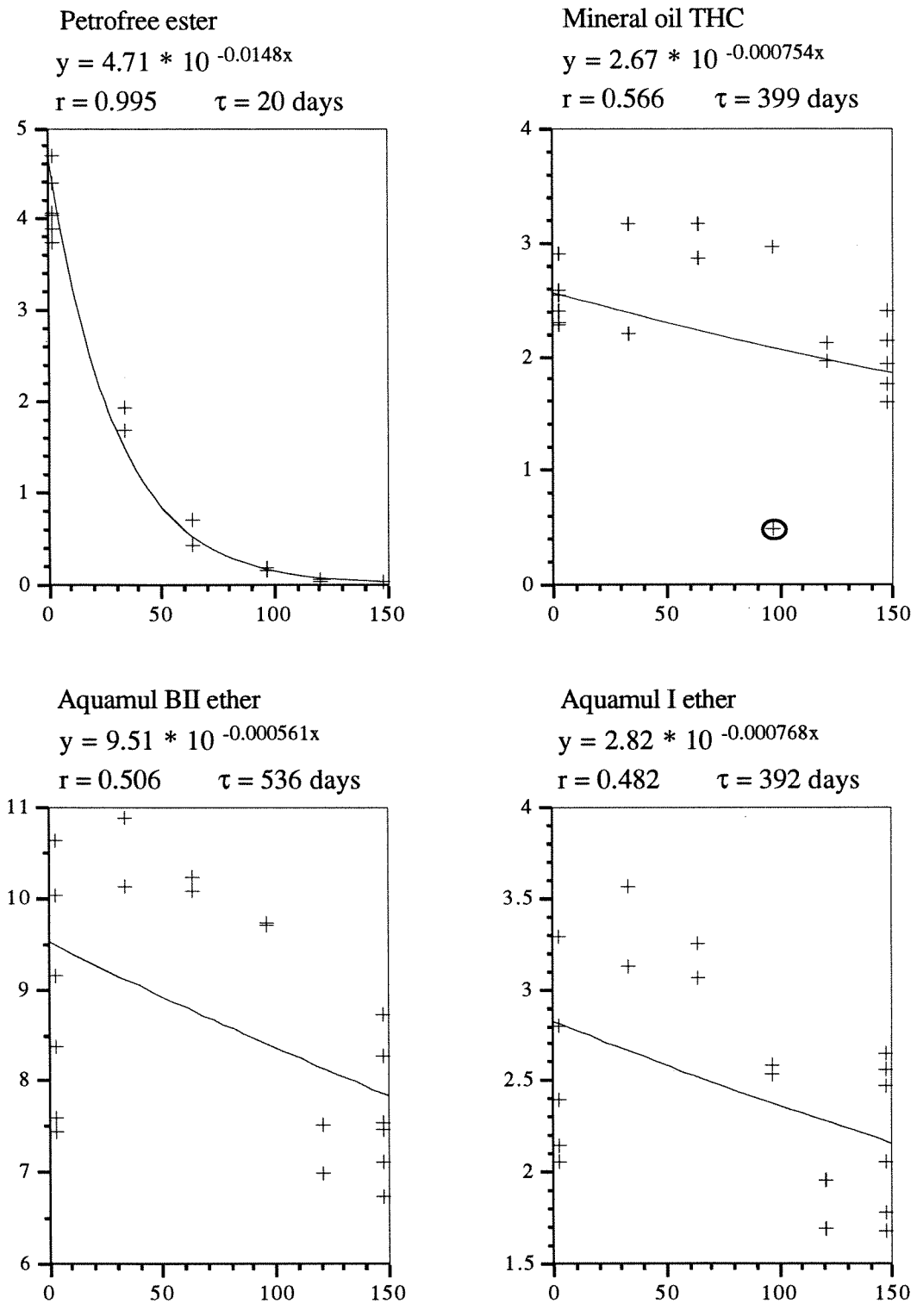

Fig. 6. Concentration of drilling fluids in sediments during the period 0-150 days after addition. Regression lines, line functions, correlation coefficients (r) and calculated half-lives are shown for each treatment. Encircled observation was omitted in the statistical analyses of the mineral oil data.

A remarkable trend of the data for mineral oil and both Aquamul ethers was that the concentrations appeared to increase during the first 30-60 days. Similar observations have been made during previous studies, but have been thought to be merely a result of large random errors. The repeated observations of the same trend seem to require some comment.

The THC is a non-specific analysis of a large number of compounds having certain common properties. Thus, although not very likely, it appears possible that compounds measured in the THC analyses might enter the sediment pool of THC from biodegradation processes in the sediment or by sedimentation or adsorption of THC from the seawater flowing through the chambers. However, the determination of Aquamul ethers is a specific gas chromatographic analysis of mostly one separate C20 compound (Appendix 2). Thus the chances are very small that an identical ether could enter the sediment pool after deposition of the cuttings.

However, it was noted that during the day zero sampling, and particularly with the Aquamul ethers, a hydrofobic film appeared to stick to the wall of the coring device. The film was not easily transferred to the sample container and may have caused some loss of drilling fluid from the sample. This problem was less pronounced during later sampling. If some kind of geochemical ageing occurr at the sediment surface after deposition, which in effect makes the drilling fluids more closely associated with sediment particles, the day zero concentrations may be underestimated as a result of a systematic higher loss of drilling fluids during the first sampling. A similar process may probably apply to any of the organic fluids added with drill cuttings.

Anyway, the concentrations of THC and Aquamul ethers did not fit very well to simple linear or exponential regression models. The data shown in fig. 6 appeared better fit to a model having an initial phase of 60-90 days with constant or slightly increasing concentrations followed by a period of a relatively rapid linear or exponential loss. In fact, most of the loss of mineral oil THC and both of the aquamul ethers was observed to occurr between day 60 and 120.

3.3 SEDIMENT OXYGEN CONSUMPTION

Results of the oxygen consumption measurements are shown in table 10 and in figs. 7 and fig. 8 below.

Table 10 shows minimum, maximum and mean values for each chamber. Because of occassional chapping of tubes at the rollers of the peristaltic pumps and leakage at the edge of the lids, table 10 reveals several missing values. Thus the number of observations, n, varied from 30 to 36. The standard deviation in the control chambers was partly a result of temperature variations causing real variations in cell metabolism, partly a result of random errors which increase with decreasing concentration difference across the chamber. The control chambers were run with a lower concentration difference than the treated chambers. The larger standard deviations in the treated chambers were primarily a result of real variations caused by the addition of cuttings.

Nevertheless, similarly treated chambers provided very similar mean and maximum rates of SOC. The reproducibility is also evident from the plot of the cumulative oxygen consumption in each chamber shown in fig. 7.

Thus, the mean oxygen consumption was 218 $\mu mol \cdot m^{-2} \cdot h^{-1}$ in the two control chambers. The Aquamul and the mineral oil treatments gave identical mean rates of 553 $\mu mol \cdot m^{-2} \cdot h^{-1}$, whereas the Petrofree treatments obtained the highest mean SOC of 889 $\mu mol \cdot m^{-2} \cdot h^{-1}$.

Table 10. Statistical analyses of observations of sediment oxygen consumption ($\mu mol \cdot m^{-2} \cdot h^{-1}$).

	2-UCON	7-TCON	3-AQII	8-AQII	4-PTF	5-PTF	1-MOM	6-MOM
Maximum	604	582	787	883	1458	1464	835	920
Minimum	61	85	213	182	214	334	95	337
Mean	210	225	516	590	883	894	493	613
Std.deviation	94	87	123	161	340	330	130	133
Number of data	30	35	36	36	35	35	35	33

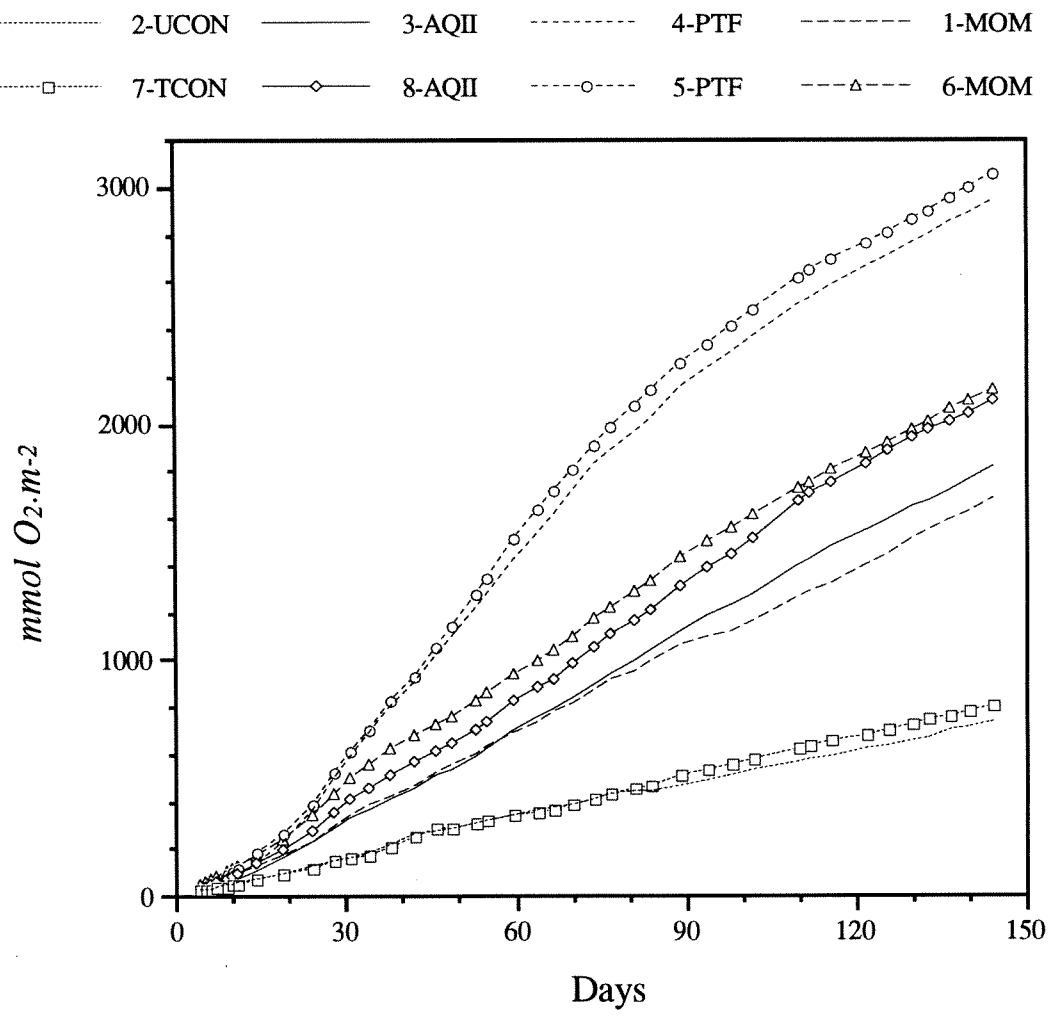

Fig. 7. Cumulative oxygen consumption in control and treated chambers.

The variations with time of the rates of oxygen consumption are shown in fig. 8. The figure displays the difference between the mean rates in similarly treated chambers and the mean rates in the control chambers. Thus fig. 8 shows primarily, the rate of oxygen consumption produced by drilling fluid decomposers.

Temperature variations in the water may have significant effects on the metabolic rates in the sediment. Thus, if temperatures increase, oxygen consumption may increase in control as well as in treated chambers. *Vice versa*, when temperatures decrease, oxygen consumption may decrease.

The general increase of oxygen consumption rates observed in all chambers during the first month co-occurred with declining temperatures from 9°C on day 0 to a minimum of 6°C at about day 40 (fig. 3). Obviously, this initial increase of SOC resulted from a

growing population of decomposers exploiting the added drilling fluids. The temporary kick-back observed at about day 40 in all chambers, controls included, most probably resulted from the introduction of colder water slowing down cell metabolism in the sediments.

From day 45 untill the end of the experiment, temperatures were more stable, declining slowly from 7.5°C to 6°C. The high SOC-rates observed at about day 30, were re-established soon after the temperature had risen to 7.5-7.8°C and remained at a high level untill day 80 in the Petrofree and mineral oil chambers. In the Aquamul chambers, which had received a much higher initial dose of drilling fluids (table 9), SOC-rates remained at a higher level for another 40-50 days.

By the end of the experiment the SOC in all chambers treated with drill cuttings were still 2-3 times higher than the SOC in the control chambers.

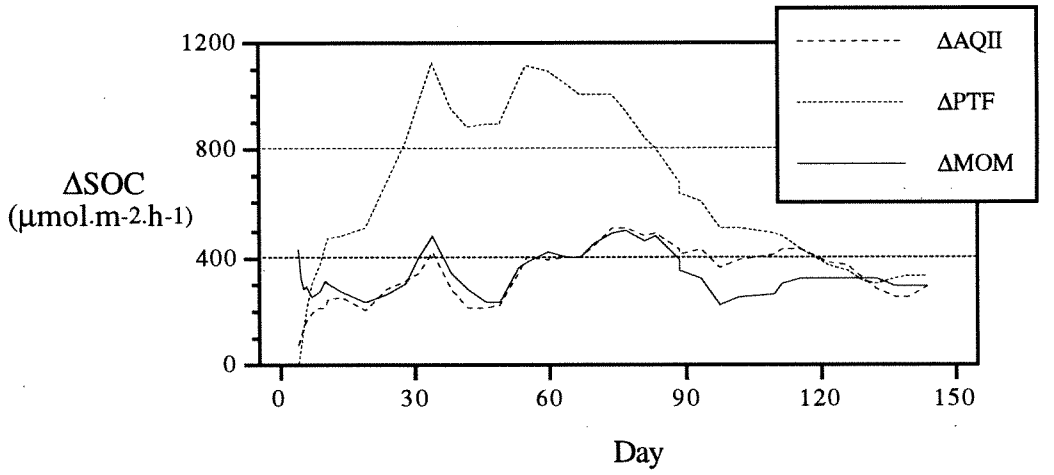

Fig.8. Mean excess sediment oxygen consumption in treated chambers from day 0 to day 150.

3.4 MASS BALANCE FOR DRILLING FLUIDS

If the drilling fluids on the cuttings deposited on the sediment surface is completely degraded to carbon dioxide by microorganisms using oxygen for respiration, biodegradation of added substance can be calculated from the equation

(eq. 3.12) $R = \Delta SOC \cdot ThOD$

in which ThOD is the theoretical oxygen demand calculated from the stoichiometry of the respective drilling fluid. Thus, a ThOD of 3.45 $gO_2 \cdot gDF^{-1}$ (DF=Drilling fluid) was used for mineral oil, 3.01 $gO_2 \cdot gDF^{-1}$ was used for Aquamul ethers and 2.97 $gO_2 \cdot gDF^{-1}$ was used for the Petrofree esters.

Table 11. Mass balance for drilling fluids in each chamber during the period 3-148 days after addition of cuttings. (Units $mg \cdot cm^{-2}$).

Chamber	PTF-4	PTF-5	MOM-1	MOM-6	AQII-3	AQII-8
Initial in sediment	4.17	4.10	2.41	2.57	11.33	11.71
- Final in sediment	0.04	0.03	2.03	1.95	10.79	9.04
= Total loss from sediment	4.13	4.07	0.38	0.61	~~0.55~~[1]	2.68
- Respired (eq.3.12)	1.81	1.91	0.76	1.15	0.88	1.11
= Other loss	2.32	2.16	-0.38	-0.54	-0.33	1.56
Total loss	99%	99%	16%	24%	~~4.9%~~[2]	23%
Loss by respiration	43%	47%	32%	45%	7.8%	9.5%
Respired relative to tot. loss	44%	47%	200%	189%	~~160%~~[3]	41%

[1]Uncertain, difference was less than standard deviation.

[2]Regression analyses of all AQII data gave a total loss of 18%.

[3]Regression analyses of all AQII data gave a respiration of 48% of total loss.

In table 11, R was calculated by eq. 3.12 using the observed increase of sediment oxygen consumption in treated relative to control chambers. The table showed that over the entire test period, 99% of the Petrofree esters were lost from the sediment as compared to 16-24% of the mineral oil THC and Aquamul ethers. The calculated loss by respiration could account for 41-48% of the total loss of ethers and esters, but was nearly twice as high as the total loss of THC. A similar ratio between respiration and loss of THC has been found in a previous study reported by Bakke et al, 1989. They concluded that the mineral oil cuttings must have contained oxygen consuming agents other than those measured by THC.

As discussed in ch. 3.2, the initial concentrations of the ethers as well as THC may have been underestimated. Thus, if we disregard the initial concentrations observed and assume that the measured concentrations on day 60 was a more accurate measure on initial concentration, the total loss of Aquamul ethers and mineral oil in the four

chambers would range between 30% in AQII-8 and 34% in MOM-I, and the loss by respiration would be 20-28% of the total loss of the ether and 72-127% of the total loss of THC. With regard to THC, then, because an average loss by respiration of 99% would be an almost ideal ratio, the respiration data strongly support the significance of the initial increase of concentrations observed in the sediments.

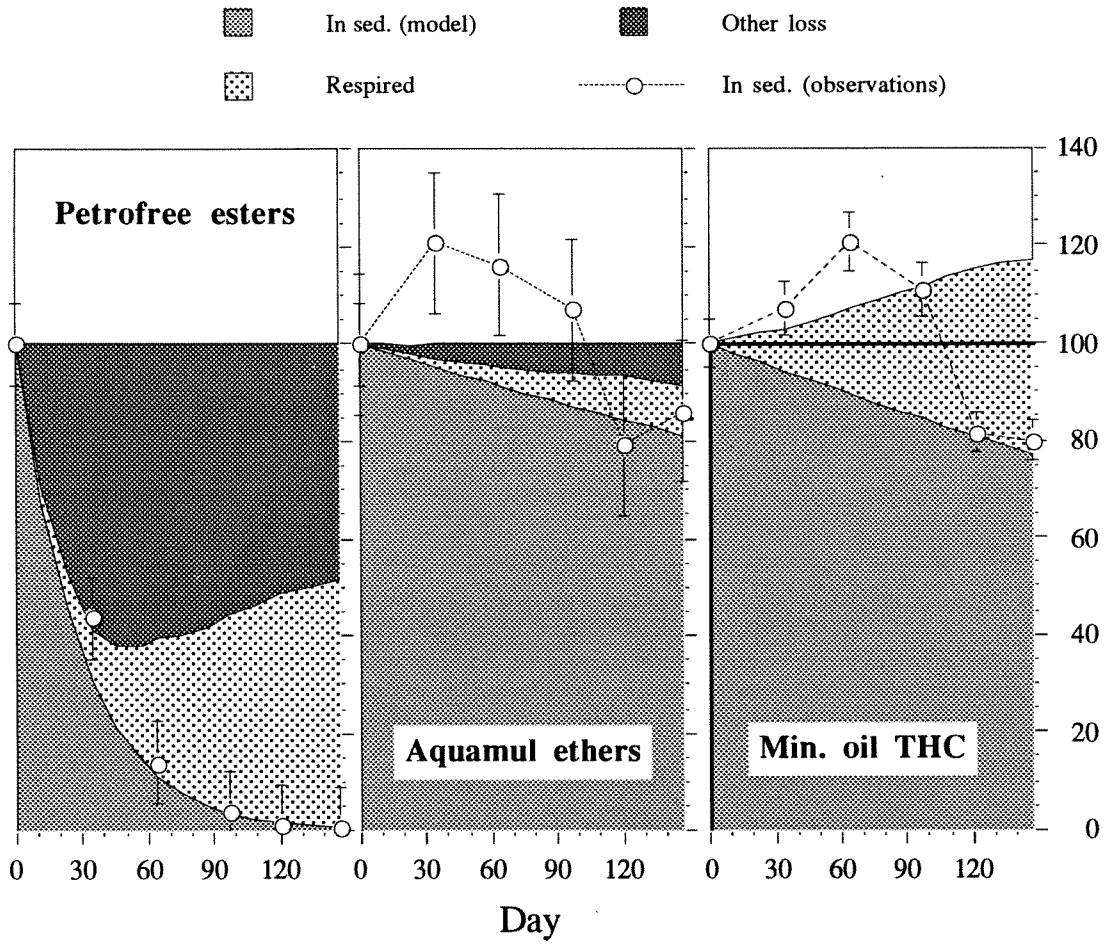

Fig. 9. Relative loss of drilling fluids by respiration and other processes. Drilling fluids remaining in sediment was calculated from the regression model shown in fig.6 (shaded area) and from actual observations (open circles). Vertical bars on the latter represent two standard deviations of the six analyses taken on day 0.

The different trends of the mass balance of the three types of cuttings, shown in fig.9, was calculated using day zero as initial concentrations. For THC, the figure shows that the sum of respired THC and THC remaining in sediment increased to 117% of the THC present on day zero. However, assuming again that the concentrations measured on day 60 was a more accurate measure on initial concentrations, the inserted curve of relative concentrations show that the data on respiration and remaining THC fits very well with the assumption of underestimated concentration data on day zero.

The trend of the mass balance of the Aquamul ether calculated from the regression cuve on all concentration data, shows a steady increase of the pool termed other loss. By the end of the experiment 80% of the ether present on day zero was still present in the sediment. Ca.10% had been respired and ca.10% was unaccounted for. However, the concentration data does not fit very well with this model. If it was assumed that the day 30 or day 60 observations were more accurate measures of initial concentrations, only ca. 60% of the Aquamul ether would remain present by the end of the experiment. Respiration would have accounted for slightly less than 10% and the unaccounted loss would increase to ca 30%. Principally this difference is not important, but the unreasonable initial increase of concentrations would be explained.

With the Petrofree esters, however, figure 9 shows the close fit between the regression model and the actual observations. A very interesting feature of the data revealed by the figure is that the unaccounted fraction reach a maximum of ca 60% at about day 45 and decrease to 50% by the end of the experiment. This was a result of a clear time-lag between loss of ester, of which 60-70% occurred during the first 30 days, and oxygen consumption, of which 80% occurred later than day 30.

The observed time-lag between loss of ester and oxygen consumption shall be further discussed below. So shall the primary difference between mineral oil, for which respiration could account for the total loss, and the synthetic fluids, which both yielded mass balance deficits of 10-50%.

4 DISCUSSION AND MAIN CONCLUSIONS

4.1 Composition of the Aquamul ether cuttings sample

Not until after the final sampling on day 150, when the chemical analyses of the sediment samples were performed, it was discovered that the cuttings sample provided by the contractor contained a significant proportion of the old Aquamul ether. A ratio of 60% of the new Aquamul BII and 40% of the old Aquamul ether product was found by analyses of the cuttings sample.

The concentration of both products were determined in all samples. Thus the test could provide a direct comparison between the rates at which the two ethers were lost from the sediments. On the other hand, mass balance considerations and effects on sediment environment could not be assigned to one product or the other.

4.2 Improved reproducibility of drilling fluid analyses

The reproducibility of the analytical methods determined by extraction and gas chromatographic analyses of spiked sediment samples were less than 4 % (appendix 2). The overall test reproducibility can never be better than the analytical reproducibility. Major variations may originate from natural variations produced by uneven sedimentation and postdepositional redistribution produced by the activity of the benthic fauna as well as from core sampling, sectioning, handling and storage of the sediment samples. Compared to well documented laboratory analyses one must accept a much lower overall precision for the test results.

In a previous experiment, the reproducibility for Petrofree esters and mineral oil THC determined as the relative standard deviation of replicate samples of the sediment surface on day zero, ranged 20-31%, but variations up to 50-100% have frequently caused a major problem in the interpretation of test results. Thus the range of reproducibilities of 8.3-14.8% obtained in the present test (table 7) showed that the modifications of the sampling strategy and the change of concentration units from $mg \cdot g^{-1}$ dry sediment to $mg \cdot cm^{-2}$ sediment area, had resulted in a major improvement with regard to test precision.

4.3 Postdepositional ageing of particle - drilling fluid associations?

Measured concentrations of mineral oil THC and Aquamul ether were observed to increase during the first 30-60 days present at the sediment surface. It was also noted that a hydrophobic film which adhered to the wall of the sampling device, was not completely transferred to the sample containers. This film, even though constituting a negligible weight fraction of the total sample, could contain significant amounts of drilling fluid. The problem was only noted with the ether samples on day zero, but may have applied to the other drilling fluids as well as on later sampling occasions.

The drilling fluids are tightly associated with the inorganic particles of cuttings and sediments. The initial treatment when making up the slurries and exposing the cuttings to the ion matrix of the sea water may alter the association between particles and drilling fluids. The observations made during the present investigation tend to suggest that an ageing process follows deposition of the cuttings slurry on the sediment surface. During this process, the drilling fluids may have become more strongly attached to the sediment fraction. Thus, a systematic loss of a fraction which shortly after deposition had a stronger affinity for the sampling devices may have caused an underestimation of the THC and Aquamul ether concentrations determined on day zero. Such an underestimation could explain the odd results of increasing concentrations during the 0-60 days period and the mismatch between respiration data and total loss of THC.

4.4 Total loss of added drilling fluids

Loss by resuspension of sediment should not occurr at the current velocities applied during the experiment. Likewise, downwards mixing to depths exceeding the sampling depth of 20 mm, have during previous Solbergstrand tests been found to be negligible. The fluids tested are not easily soluble in water and any loss of soluble components should occur during test preparation prior to determination of the initial concentration. Thus, if the loss from the sediments by resuspension, bioturbation and dissolution did not account for any significant loss of drilling fluids, any loss should be considered a result of enzymatic reactions occurring in the sediment to alter the properties of the drilling fluids.

The concentration of Petrofree esters in the sediment decreased exponentially with time with a halflife of 20.3 days. This was in good agreement with previous test results.

Regression analyses of the concentrations of both types of Aquamul ethers and mineral oil THC showed a loss of all drilling fluids. In spite of the possible underestimation of the concentrations measured on day zero, the loss was significant at the 95% significance level. However, the fact that the degradation curves were poorly correlated with simple linear or exponential regression models may have resulted from systematic analytical errors in the early samples or from a real lag phase of 30-60 days preceding a phase of rapid linear or exponential degradation.

The halflives calculated from the exponetial models were 399 days for THC, and 392 and 536 days for the Aquamul and Aquamul BII ethers, respectively. These values were rather uncertain and the internal variation are may reflect initial differences in concentration rather than real differences in degradation behaviour. However, the loss of both Aquamul ethers and mineral oil THC was in an order of ten times or more, slower than the loss ef the Petrofree esters.

4.5 Biodegradation of Petrofree esters

The Petrofree esters will most likely undergo a hydrolytic cleavage to yield a C10-C14 saturated fatty acid and 2-ethyl hexanol. The alcohol is readily dissolved in water and neither product will be determined in the ester analyses. Thus, mineralisation can be considered a two-step process. If the hydrolytic reaction is fast compared to biodegradation and loss of metabolites, an accumulation of alcohol and fatty acid metabolites should occur.

The test setup was not designed to study the most early phase of degradation. Oxygen consumption measurements were not reliable untill 7-8 days after the addition of the cuttings to the chambers and 4-5 days after the initial sampling of the sediment. However, the increase of oxygen consumption relative to control chambers, showed that biological processes were involved in the decomposition of all drilling fluids from at least 4-5 days after the determination of the initial concentrations.

Thus biological processes appears to have been involved also in the hydrolytic cleavage of the Petrofree esters. However, the oxygen consumed during this initial splitting of the carbon chains, should be much less than the loss of ester, as was indeed observed during the first 30 days period (fig. 9).

Thus, the sequence of ester biodegradation explaining the observations shown in fig.9 should be as follows: Rapid hydrolytic cleavage of the ester bonds provided an increasing pool of metabolites during the first 30-60 days. When the concentration of metabolites increased a growing population of decomposers caused a corresponding increase of the rates of oxygen consumption. When the ester reservoir was depleted at about day 60, production of metabolites seized. However, because of the accumulated reservoir of ester metabolites, oxygen consumption remained high until the metabolites could no longer support an oversized population of decomposers. This occurred at about day 80. Decomposition of more refractory metabolites, decomposer tissues and oxidation of reduced sulphide, ferrous iron and other inorganic compounds (eqs. 3.7, 3.8, 3.10) may sustain a lower but still elevated rate of oxygen consumption for an unknown period of time.

Thus, by the end of the experimental period, oxygen consumption was still 2-3 times higher in Petrofree as compared to control chambers. Because there were no more esters left in the sediment, the mismatch between accumulated SOC and total loss of esters will continue to diminish. The ultimate magnitude of the mismatch should primarily depend on the loss to the watermass of ester metabolites and the amount of reduced compounds (refractory organic carbon and reduced inorganic species), which have been permanently incorporated in the sediment.

In the two-step mineralisation model, biodegradation of the metabolites appeared to be rate-limiting. The observed degradation curve (eq.3.11) describe the hydrolytic cleavage reaction. Thus, in spite of a half-life of 20 days for the mother-compound, complete mineralisation to CO_2 could only account for 50% of the added ester carbon (see fig. 9) over the 150 days experimental period. The fate and environmental effects of the remaining 50% is not known. It can be speculated that this unaccounted fraction is dominated by the more soluble and less bioavailable alcohols (as compared to fatty acids) leaking out of the sediments.

4.6 Biodegradation of mineral oil THC and Aquamul ether

Like the ester, the degradation of the Aquamul ether can be modelled as a two-step reaction involving an initial hydrolytic cleavage of the ether bond followed by biodegradation of the metabolites. Hydrolyzes of ethers yield mostly alcohols.

The slow loss of the ether showed that the hydrolytic cleavage of the Aquamul ether is a much slower process than the cleavage of the Petrofree esters. Neither was the

cleavage of the Aquamal IIB ether significantly faster than the cleavage of the Aquamul B ethers.

Because environmental effects of the ester degradation appeared to be primarily related to the decomposition of a large pool of rapidly produced and easy degradable metabolites, it might be interesting to assess possible differences with regard to the fate and degradability of the metabolites.

The mass balance deficit of 50% of the ester carbon may have resulted from slowly degrading or refractory organic carbon remaining in the sediment, as well as organic compounds which had escaped to the watermass. As argued in ch. 3.1.4 an 3.4, reduced iron and sulfur species may also contribute to some of the ester deficit. Such contributions are probably negligible in the other treatments were pore waters remained non-sulphidic throughout the experiment.

Also the Aquamul ether budget showed a deficit of 50-80% of the decomposed ether. Like with the ester this deficit may have been constituted by refractory compounds present in the sediment or more soluble components which had leaked into the overlying water. Unlike the ester, however, none of the metabolites of ether were degraded as fast as the ester metabolites. This may have resulted from the much slower production of ether metabolites, but it might also have resulted from the fact that fatty acids is a more frequent product of ester hydrolyses. Perhaps the intensive biodegradation observed during the 30-80 days period in the Petrofree treatments was the result of intensive utilisation of a pool of fatty acids derived from the esters. Thus, whereas fatty acids are rapidly exploited by the decomposers, more soluble alcohols may have been lost to the watermass or less soluble alcohols may have remained in the sediment. Slowly degradable alcohols present in the sediments might indeed have been the substrate supporting the moderate rates of oxygen consumption observed in Petrofree as well as in the Aquamul chambers towards the end of the study. Wether leaking to the watermass or remaining in the sediment, the alcohols would not show up in the chemical analyses of the respective esters and ethers. Therefore, the mass balance deficit in both treatments should be expected.

The mineral oil THC was lost at a rate similar to the loss af the Aquamul ether and similar oxygen consumption rates indicated similar levels of decomposer activity. Thus, one might hypothesize that a similar two step reaction involving an initial slow cleavage of the more heterogenous mineral oil components, followed by biodegradation of the metabolite compounds. The data gave no evidence for the presence of any metabolites of the initial mineral oil THC, but the mass balance showed that if

metabolites had been produced they were either degraded as fast as they had been produced or they were still present in the sediment and measured as THC by the end of the experiment.

4.7 Environmental effects of biodegradation of drilling fluids

The various drilling fluids produced very different effects on the environment at the sediment water interface. An initial rise of the pH in the Aquamul treatments revealed the presence of mineral buffers such as calcium hydroxides or carbonates. This was the only significant non-biological effect observed on the environment. The effect was negligible after day zero and the maximum pH deviation did not perturb any environmental quality criteria.

The Petrofree ester cuttings produced a much stronger stimulation of total sediment metabolism than Aquamul ether and mineral oil cuttings. The rates of oxygen consumption in the Petrofree ester treatments increased to maximum rates of 1400 $mgO_2 \cdot cm^{-2}$ in the Petrofree treatments as compared to 800 $mgO_2 \cdot cm^{-2}$ in Aquamul and mineral oil treatments. In the control chambers a more or less stable level of 200-250 $mgO_2 \cdot cm^{-2}$ was observed throughout the experimental period. The rates in the Petrofree treatments slowed down 80 days after addition. The slow down in the mineral oil and Aquamul treatments occurred somewhat later and were less pronounced. By the end of the experiment, oxygen consumption rates had leveled out at about 500 $mgO_2 \cdot cm^{-2}$ in all treated chambers. Because however, of the smaller remaining reservoir of organic carbon in the Petrofree ester treatments, oxygen consumption rates would be likely to remain at this moderately elevated level for a longer period of time in the Aquamul and mineral oil treatments.

The stimulated sediment metabolism produced a slight lowering of the pH and redox potentials in all treatments. A major drop of the redox potential in the Petrofree treatments 60 days after addition of the cuttings and a subsequent drop of pH showed an episodic presence of hydrogen sulphide resulting from the rapid degradation of the esters. Because of the extreme toxicity of the hydrogen sulphide, such conditions are intolerable to many benthic species. Some species may survive through their ability to exploit oxygen reservoirs in tubes, burrows and overlying water, but any prolonged impact would have dramatic effects on all animals living in or at the sediment surface.

At the deposition sites in the North Sea the choice between the Aquamul ether and the Petrofree ester appears to be the choice between dramatic effects of biodegradation over a smaller area for a shorter period of time and moderate effects over a larger area for a longer period of time.

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APPENDIX 1: Tables of results.

Table A1. *In situ* measurements of pH and redox potentials.

		pH			Eh (mV)		
Depth (mm)		5	15	25	5	15	25
Treatment	S.no						
Day 0							
UCON2	1	7.64	7.37	7.24	173	129	82
UCON2	2	7.51	7.34	7.18	159	96	56
UCON2	3	7.58	7.33	7.22	117	77	0
TCON7	1	7.59	7.36	7.29	203	173	147
TCON7	2	7.84	7.57	7.33	217	165	130
TCON7	3	7.89	7.65	7.31	193	155	124
MOM 1	1	7.72	7.56	7.45	213	115	58
MOM 1	2	7.74	7.51	7.39	165	106	64
MOM 1	3	7.57	7.42	7.29	147	74	-9
MOM 6	1	7.54	7.40	7.33	147	107	42
MOM 6	2	7.59	7.44	7.31	113	28	8
MOM 6	3	7.54	7.41	7.30	108	57	22
PTF 4	1	7.50	7.30	7.19	117	33	1
PTF 4	2	7.44	7.32	7.25	72	-1	-25
PTF 4	3	7.47	7.34	7.24	119	57	18
PTF 5	1	7.60	7.43	7.35	128	99	69
PTF 5	2	7.58	7.39	7.28	159	39	75
PTF 5	3	7.60	7.43	7.30	152	112	78
AQII 3	1	8.66	8.38	7.88	117	77	47
AQII 3	2	8.59	8.49	8.04	107	62	35
AQII 3	3	8.54	8.17	7.96	117	72	45
AQII 8	1	8.41	8.17	7.97	109	59	16
AQII 8	2	8.24	8.20	7.81	75	19	-13
AQII 8	3	8.33	8.02	7.74	36	21	-7
Day 30							
UCON2	1	8.01	7.77	7.45	143	75	46
UCON2	2	7.86	7.55	7.35	130	94	54
UCON2	3	7.77	7.52	7.31	142	102	66
TCON7	1	8.05	7.70	7.40	132	101	70
TCON7	2	7.89	7.63	7.34	130	87	55
TCON7	3	7.85	7.54	7.28	139	105	77
MOM 1	1	7.63	7.28	7.15	110	36	16
MOM 1	2	7.66	7.35	7.25	95	57	39
MOM 1	3	7.59	7.35	7.14	89	56	32
MOM 6	1	7.74	7.59	7.47	106	93	92
MOM 6	2	7.58	7.41	7.32	95	89	79
MOM 6	3	7.58	7.48	7.41	83	72	56
PTF 4	1	7.67	7.53	7.47	107	103	93
PTF 4	2	7.60	7.45	7.37	74	80	84
PTF 4	3	7.56	7.45	7.37	97	94	83
PTF 5	1	7.61	7.48	7.42	58	80	82
PTF 5	2	7.48	7.33	7.26	70	98	96
PTF 5	3	7.53	7.42	7.35	-26	-37	-43
AQII 3	1	7.83	7.51	7.28	-16	-21	-19
AQII 3	2	7.87	7.47	7.34	19	-2	-13
AQII 3	3	7.76	7.41	7.22	80	62	39
AQII 8	1	7.88	7.69	7.51	-91	-14	-42
AQII 8	2	7.91	7.73	7.57	33	18	-2
AQII 8	3	7.86	7.67	7.46	45	21	-3

Day 60							
UCON2	1	7.81	7.53	7.31	101	51	2
UCON2	2	7.80	7.52	7.32	167	130	81
UCON2	3	7.73	7.48	7.29	156	127	92
TCON7	1	7.66	7.43	7.29	164	135	120
TCON7	2	7.82	7.59	7.41	152	133	121
TCON7	3	7.76	7.56	7.36	162	134	115
MOM 1	1	7.86	7.47	7.21	183	148	130
MOM 1	2	7.83	7.46	7.18	180	115	101
MOM 1	3	7.58	7.30	7.19	96	94	99
MOM 6	1	7.55	7.36	7.20	6	-4	-22
MOM 6	2	7.61	7.35	7.14	82	58	31
MOM 6	3	7.62	7.43	7.31	78	36	-77
PTF 4	1	7.51	7.43	7.39	19	-142	-151
PTF 4	2	7.59	7.52	7.46	-161	-190	-197
PTF 4	3	7.55	7.50	7.44	-168	-191	-200
PTF 5	1	7.58	7.50	7.44	-62	-70	-83
PTF 5	2	7.59	7.49	7.43	-148	-190	-196
PTF 5	3	7.52	7.43	7.34	-183	-197	-200
AQII 3	1	7.84	7.47	7.24	80	-	-
AQII 3	2	7.79	7.53	7.29	115	100	88
AQII 3	3	7.84	7.60	7.45	126	106	95
AQII 8	1	7.88	7.68	7.49	91	86	69
AQII 8	2	7.88	7.52	7.35	82	37	-3
AQII 8	3	7.81	7.54	7.39	87	42	-48
Day 90							
UCON2	1	7.98	7.64	7.47	148	116	86
UCON2	2	8.00	7.76	7.58	197	136	111
UCON2	3	7.75	7.47	7.35	162	113	69
TCON7	1	7.88	7.78	7.59	183	143	117
TCON7	2	7.79	7.62	7.42	183	135	112
TCON7	3	7.87	7.71	7.49	198	144	121
MOM 1	1	7.72	7.53	7.40	121	98	81
MOM 1	2	7.69	7.47	7.30	108	98	91
MOM 1	3	7.61	7.42	7.33	97	88	78
MOM 6	1	7.72	7.46	7.35	162	121	109
MOM 6	2	7.69	7.43	7.27	117	99	90
MOM 6	3	7.74	7.49	7.38	118	85	80
PTF 4	1	7.56	7.26	7.12	96	98	82
PTF 4	2	7.68	6.98	6.87	76	85	59
PTF 4	3	7.13	6.86	6.84	80	69	54
PTF 5	1	7.29	7.16	7.05	118	105	97
PTF 5	2	7.45	7.31	7.24	32	26	31
PTF 5	3	7.31	7.13	7.09	81	78	69
AQII 3	1	7.73	7.57	7.32	123	97	89
AQII 3	2	7.76	7.53	7.40	106	83	77
AQII 3	3	7.76	7.48	7.38	102	87	81
AQII 8	1	7.81	7.58	7.45	122	112	91
AQII 8	2	7.88	7.69	7.55	199	110	100
AQII 8	3	7.75	7.54	7.35	106	88	83

Day 120							
UCON2	1	7.69	7.51	7.28	192	76	91
UCON2	2	7.71	7.42	7.23	164	117	88
UCON2	3	7.82	7.61	7.44	193	143	123
TCON7	1	7.80	7.57	7.44	217	157	124
TCON7	2	7.90	7.75	7.56	225	140	123
TCON7	3	7.81	7.59	7.40	221	164	139
MOM 1	1	7.81	7.46	7.27	214	157	129
MOM 1	2	7.68	7.36	7.17	124	118	106
MOM 1	3	7.54	7.12	7.03	127	108	94
MOM 6	1	7.64	7.37	7.18	-65	36	55
MOM 6	2	7.54	7.33	7.22	136	104	92
MOM 6	3	7.47	7.28	7.15	135	115	99
PTF 4	1	7.52	7.25	7.14	173	131	91
PTF 4	2	7.57	7.21	7.06	192	127	100
PTF 4	3	7.61	7.07	6.82	96	44	43
PTF 5	1	7.52	7.13	6.83	185	165	154
PTF 5	2	7.50	7.08	6.92	192	142	130
PTF 5	3	7.46	7.00	6.71	157	132	119
AQII 3	1	7.63	7.34	7.15	159	112	101
AQII 3	2	7.70	7.50	7.41	92	82	82
AQII 3	3	7.71	7.44	7.31	118	91	82
AQII 8	1	7.62	7.41	7.24	137	99	88
AQII 8	2	7.74	7.47	7.37	145	94	67
AQII 8	3	7.67	7.55	7.45	128	91	82
Day 150							
UCON2	1	7.80	7.68	7.54	224	167	150
UCON2	2	7.86	7.68	7.37	152	137	133
UCON2	3	7.79	7.55	7.45	206	177	167
TCON7	1	7.85	7.69	7.47	214	178	146
TCON7	2	7.89	7.73	7.57	214	180	160
TCON7	3	7.85	7.69	7.57	205	156	139
MOM 1	1	7.62	7.45	7.32	165	152	136
MOM 1	2	7.62	7.34	7.21	128	120	115
MOM 1	3	7.65	7.41	7.25	149	113	104
MOM 6	1	7.65	7.46	7.41	178	145	123
MOM 6	2	7.62	7.48	7.38	152	134	130
MOM 6	3	7.66	7.43	7.34	149	134	117
PTF 4	1	7.68	7.49	7.41	-	199	169
PTF 4	2	7.72	7.52	7.39	179	206	145
PTF 4	3	7.71	7.58	7.50	133	124	112
PTF 5	1	7.47	7.23	7.22	195	156	135
PTF 5	2	7.75	7.35	7.19	163	151	41
PTF 5	3	7.69	7.31	7.16	-	-	-
AQII 3	1	7.73	7.54	7.41	189	10	69
AQII 3	2	7.73	7.51	7.41	112	92	-
AQII 3	3	7.71	7.52	7.38	109	62	37
AQII 8	1	7.75	7.60	7.47	167	132	124
AQII 8	2	7.67	7.58	7.36	122	113	115
AQII 8	3	7.81	7.68	7.57	144	107	95

Table A2. Concentration of drilling fluid in sediment samples measured as weight of the respective chemical per weight of dry sediment (left-hand column) and per sediment surface area (right-hand column).

Treament	Concentration	
	$mg \cdot kg^{-1}$	$mg \cdot cm^{-2}$
Day 0, 29.10.93		
PTF 5	4310	4.39
PTF 5	3640	4.04
PTF 5	3780	3.88
PTF 4	4310	4.68
PTF 4	3790	4.07
PTF 4	3410	3.75
PTF Mean	3873	4.13
PTF Std.dev.	365	0.34
PTF Rel. std.dev.	0.094	0.083
MOM 1	2080	2.57
MOM 1	1880	2.26
MOM 1	2000	2.39
MOM 6	2100	2.28
MOM 6	2640	2.53
MOM 6	2810	2.89
MOM Mean	2252	2.49
MOM Std.dev.	379	0.23
MOM Rel. std.dev.	0.168	0.094
AQBII 3	10600	10.72
AQBII 3	8320	8.44
AQBII 3	7660	7.51
AQBII 8	9910	10.10
AQBII 8	6940	9.24
AQBII 8	9160	7.66
AQBII Mean	8765	8.95
AQBII Std.dev.	1384	1.31
AQBII Rel. std.dev.	0.158	0.146
AQB3	2770	2.80
AQB3	2360	2.39
AQB3	2180	2.14
AQB8	2750	2.80
AQB8	2460	3.28
AQB8	2460	2.06
AQBMean	2497	2.58
AQBStd.dev.	228	0.47
AQBRel. std.dev.	0.091	0.181
Day 30, 29.11.93		
PTF 4	683	1.94
PTF 5	591	1.68
MOM 1	798	2.20
MOM 6	1120	3.16
AQBII 3	3760	10.21

	AQBII 8	3970	10.97
	AQB3	1150	3.12
	AQB8	1290	3.564
Day 60,	28.12.93		
	PTF 4	261	0.720
	PTF 5	160	0.446
	MOM 1	1150	3.15
	MOM 6	999	2.85
	AQBII 3	3860	10.17
	AQBII 8	4010	10.32
	AQB3	1160	3.06
	AQB8	1260	3.24
Day 90,	31.1.94		
	PTF 4	57	0.150
	PTF 5	64	0.175
	MOM 1	1090	2.94
	MOM 6	184	0.49
	AQBII 3	3610	9.79
	AQBII 8	3780	9.80
	AQB3	949	2.57
	AQB8	978	2.53
Day 120	24.2.94		
	PTF 4	19	0.051
	PTF 5	16	0.043
	MOM 1	805	2.10
	MOM 6	925	1.95
	AQBII 3	2890	7.07
	AQBII 8	3060	7.59
	AQB3	692	1.69
	AQB8	788	1.95
Day 150,	24.3.94		
	PTF 5	15	0.039
	PTF 5	11	0.030
	PTF 5	11	0.030
	PTF 4	13	0.033
	PTF 4	14	0.036
	PTF 4	14	0.036
	PTF Mean	13.0	0.034
	PTF Std.dev.	1.7	0.003
	PTF Rel. std.dev.	0.129	0.103
	MOM 1	900	2.39
	MOM 1	771	1.94
	MOM 1	640	1.75
	MOM 6	789	2.14
	MOM 6	853	2.14
	MOM 6	602	1.58
	MOM Mean	759	1.99
	MOM Std.dev.	117	0.29

MOM Rel. std.dev.	0.154	0.148
AQBII 3	3470	8.80
AQBII 3	3510	8.35
AQBII 3	2820	7.54
AQBII 8	2960	7.60
AQBII 8	2690	7.19
AQBII 8	2490	6.80
AQBII Mean	2894	7.71
AQBII Std.dev.	385	0.74
AQBII Rel. std.dev.	0.133	0.096
AQB3	1010.00	2.56
AQB3	1110.00	2.64
AQB3	924.00	2.47
AQB8	798.00	2.05
AQB8	631.00	1.69
AQB8	652.00	1.78
AQBMean	823	2.20
AQBStd.dev.	200	0.41
AQBRel. std.dev.	0.242	0.188

APPENDIX 2: SINTEF-SI report on chemical analyses

SINTEF

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REPORT

TITLE

Test on Degradation of Aquamul B II Drill Mud on Cuttings under Simulated Seabed Conditions

AUTHOR(S)

Frøydis Oreld

CLIENT(S)

NIVA

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ABSTRACT

The report presents the results of determination of Aquamul B II ether, total hydrocarbons and Petrofree esters content in sediment samples.

KEYWORDS	ENGLISH	NORWEGIAN
GROUP 1	Chemistry	Kjemi
GROUP 2	Analysis	Analyse
SELECTED BY AUTHOR(S)	Ether	Eter
	Hydrocarbons	Hydrokarboner
	Degradation	Nedbrytning

TABLE OF CONTENTS

1.INTRODUCTION

New drill mud types are investigated by the oil companies to find suitable substitutes for the base oil at present in use in the drill mud.

"Aquamul B II" is a new drill mud type where alkyl ether is a substitute for base oil. Tests to investigate the degradability and environmental effects of cuttings from drilling with Aquamul B II have been performed at the NIVA Marine Research Station at Solbergstrand.

The chemical analyses of sediment samples with regard to the content of Aquamul B II ether have been performed by SINTEF OSLO on request from Norwegian Institute for Water Research (NIVA).

The investigation also includes tests with Mineral oil cuttings and Petrofree cuttings. These have been tested at the same time for comparisons.

The present report presents the methods and results of the chemical analyses of Aquamul B II ether, Petrofree esters and total oil hydrocarbons.

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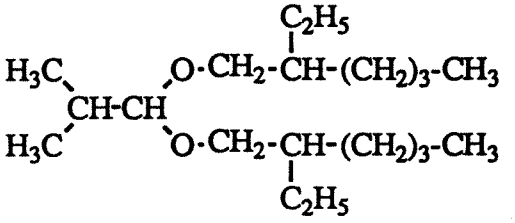
2. AQAMUL B II

DESCRIPTION OF THE ANALYTICAL PROCEDURE, QUALITY ASSURANCE PROGRAMME AND THE RESULTS OF THE AQUAMUL B II ETHER ANALYSES

2.1 ANALYTICAL PROCEDURE

2.1.1 Identity of Aquamul B II

A sample of Aquamul B II was available from Anchor Drilling Fluids. The product specifications state that the chemical is a liquid ether with a purity of 60-100% alkyl ether ($C_{20}H_{42}O_2$). In a telefax from Anchor Drilling Fluids A/S (Monica Slater) dated 27.10.93, the chemical formula of Aquamul B II was stated to be:



To confirm the chemical identity, a sample of the received Aquamul B II liquid was analysed by gas chromatography-mass spectrometry (GC/MS). The analysis confirmed that the liquid Aquamul B II consists of one main compound with a mass spectrum that agrees with the above formula.

2.1.2 Work-up procedure

The chemical analysis includes determination of the Aquamul B II ether content in sediments samples. An account of the quality assurance programme for the chemical analyses is given below.

The sediment workup procedure is based on a Soxhlet extraction method applied at the Herriot-Watt University in Scotland (Herriot-Watt, Statfjord environmental Survey, June 1984, Report to Mobil Exploration Norway Inc.).
Wet sediment samples weighing 15-20 g were homogenized and placed in a Soxhlet tube. Internal standard, dioctylether was added. The tube was refluxed with 70 ml methanol for 2.5 h. The methanol was then decanted and the sample was further extracted by refluxing with 80 ml dichloromethane over night (17 h.). The methanol extract was diluted with 70 ml of water and extracted twice with dichloromethane (40+30 ml). The dichloromethane extracts were combined, washed with 2x50 ml of water and dried over sodium sulfate. The sediment extracts were then evaporated to a suitable volume and analysed by GC.

An aliquote of the wet homogenized sediment was weighed out for determination of the dry weight and dried for 48 hours at 105°C

2.1.3 Determination of Aquamul ether content

The Aquamul B II liquid consists of one main compound, an alkyl ether (see page 5) while the sediment samples received from the Aquqmul boxes at Solbergstrand appeared to content a mixture of both Aquamul B II and Aquamul B. Aquamul B is a complex mixture of didecyl ether isomers (SI report 910433-1 February 1992). The Aquamul ether levels, both Aquamul B II and Aquamul B were determined by gas chromatography. Quantitation was carried out by measuring the flame ionization detector response of the alkyl ether Aquamul B II and the retention window for the didecyl ethers Aquamul B. The areas were compared to the corresponding response of known amounts of an internal standard, dioctyl ether.

The GC analyses were carried out under the following conditions:

Gas chromatograph	: HP 5880 with HP auto sampler Mod 7673B1
Column	:12.5 m x 0.20 mm i.d., fused silica, cross-linked with dimethyl silicone
Temperatures	
Column	: 50°C (3 min) - 20°C/min - 350°C (10 min)
Injector	: 280°C
Detector	: 350°C
Carrier gas	: Hydrogen
Injection volume	: 1 µl
Data system	: Turbochrom 3

Typical gas chromatograms are shown in Figure 2.1 - 2.2.

2.2 QUALITY ASSURANCE PROGRAMME

2.2.1 Preparation of samples and equipment

Trace analysis requires control of the background levels of chemicals and equipment. All chemicals are therefore purified prior to use. In addition, the total analytical procedure is checked at regular intervals by routinely analysing procedural blanks.

HPLC grade dichloromethane, hexane and methanol are used. All equipment is rinsed with dichloromethane and heated at 600°C over night. Cleaned equipment is kept wrapped in aluminium foil.

The instruments are regularly calibrated using appropriate standards and instrument performance is checked at regular intervals.

2.2.2 Accuracy

An internal standard dioctyl ether was added to the sediment samples prior to the extraction procedure to compensate for losses during the sample preparation. The accuracy of the method was checked by spiking non-contaminated sediments with known amounts of Aquamul B II at 3000 ppm concentration level. An average recovery of 102% was obtained after work up and analysis of three replicate samples.

2.2.3 Reproducibility

The reproducibility of the analytical procedure was determined by analyses of sediment samples spiked with known amounts of Aquamul B II ether. From three replicate sediments samples spiked with Aquamul B II a relative standard deviation of 2.5% was obtained for the alkyl ether determination.

The reproducibility of the instrumental analysis (GC) of Aquamul ether was determined by analysing a standard solution consisting of Aquamul ether and the internal standard. The Aquamul standard was analysed together with the 20 samples. Three Aquamul standards were analysed followed by the 6 samples from day 0. Two Aquamul standards were analysed after every six sample. This gave a total of nine Aquamul standards. The relative standard deviation between the 9 analysed Aquamul standards was 2.8%.

2.2.4 Quantitation limit

In these experiments the quantitation limit for Aquamul B II was set to 10 mg/ kg dry sediment.

2.3 AQUAMUL ETHER - RESULTS AND DISCUSSION

2.3.1 Content of Aquamul ether in sediments from the Aquamul trays

The results from the analyses of the content of Aquamul ether in sediment samples collected in the two Aquamul trays are given in Table 2.1 and Table 2.2. Table 2.1 gives the separate results of the content of both Aquamul B II and Aquamul B in the sediments. Table 2.2 gives the results of the sum of Aquamul B II and Aquamul B content in the sediments.

At intervals (day 0, 31, 61, 94, 118 and 145) samples were taken for Aquamul analyses. The samples were collected at random. At day 0 and day 145 three replicate samples were taken from each of the two Aquamul trays. At day 31 61, 94 and day 118 one sample was taken from each of the two Aquamul trays.

On day 0 a sediment layer of 0-1 cm was collected of all the samples. On the remaining sampling days a sediment layer of 0-2 cm was collected. This has to be taken into consideration during the interpretation of the results because sampling a thicker sediment layer will result in a dilution of the Aquamul ether in the sediment samples.

Figure 2.1 and 2.2 show a gas chromatogram of a mixture of Aquamul B II and Aquamul B spiked with dioctyl ether (internal standard). together with gas chromatograms of Aquamul sediments extracts from day 0, day 31, day 61, day 94, day 118 and day 145.

2.3.2 Discussion

Environmental surveys around the platforms in the North Sea has so far mainly been limited to elements and hydrocarbons due to use of oil based drilling mud. New types of drilling mud are now produced, and are come into use at some of the well sites. This will demand new analytical procedures dependent on the chemical used.

In the present study the Aquamul B II mud liquid consists of alkyl ether. A suitable analytical programme was set out to take care of these ether compounds. The procedure includes ectraction of the sediment samples by both a polar and an unpolar solvent and instrumental analyses of the extract by gas chromatography. Quantitation is performed by use of an internal standard added to the sediments prior to work up.

The analytical procedure worked quite well. For spiked samples at a concentration of 3000 ppm Aquamul B II ether, 102% of the real value was found, and the relative standard deviation of three replicates was 2.5 %.

The results from the analysis of Aquamul listed in Table 2.1 and 2.2 indicate that a minor reduction in the Aquamul content, both Aquamul B II and Aquamul B has taken place from day 31 to day 145 (0-2 cm sediment layer is sampled in both cases).

However, statistically treatment of the Aquamul results showed that at a 95% confidence level there is a signinficant reduction of Aquamul B II from day 0 to day 145. For Aquamul B the reduction was not significant at a 95% confidence level. (Telefax from Morten Schaanning, NIVA dated 11.05.94).

Table 2.1

CONTENT OF AQUAMUL B II AND AQUAMUL B IN SEDIMENTS
(mg/kg dry sediment)

Sample	Box no. / Sample no.	Day 0 (29.10.93) Aqu B II/ Aqu B	Box no	Day 31 (29.11.93) Aqu B II/ Aqu B	Box no	Day 61 (29.12.93) Aqu B II/ Aqu B
AQUM	3-1	10500/ 2770	3	3720/ 1150	3	3830/ 1160
	3-2	8240/ 2360	8	3930/ 1290	8	3970/ 1260
	3-3	7590/ 2180				
	8-1	9810/ 2750				
	8-2	6870/ 2460				
	8-3	9070/ 2460				
mean		**8680/ 2497**		**3825/ 1200**		**3900/ 1210**

Table 2.1 (continued)

Sample	Box no.	Day 94 (31.01.94) Aqu B II/ Aqu B	Box no	Day 118 (24.02.94) Aqu B II/ Aqu B	Box no. / Sample no.	Day 145 (23.03.94) Aqu B II/ Aqu B
AQUM	3	3580/ 949	3	2890/ 692	3-1	3430/ 1010
	8	3740/ 978	8	3030/ 788	3-2	3480/ 1110
					3-3	2790/ 924
					8-1	2930/ 798
					8-2	2660/ 631
					8-3	2470/ 652
mean		**3660/ 964**		**2960/ 740**		**3010/ 854**

Day 0 0-1 cm sediment layer was collected.
On the remaining days sediment layer of 0-2 cm was collected.

Table 2.2

CONTENT OF SUM AQUAMUL B II AND AQUAMUL B IN SEDIMENTS
(mg/kg dry sediment)

Sample	Box no. / Sample no.	Day 0 (29.10.93) Sum Aquamul	Box no	Day 31 (29.11.93) Sum Aquamul	Box no	Day 61 (29.12.93) Sum Aquamul
AQUM	3-1	13300	3	4870	3	4990
	3-2	10600	8	5210	8	5230
	3-3	9760				
	8-1	12600				
	8-2	9330				
	8-3	11600				
mean		**11198**		**5040**		**5110**

Table 2.2 (continued)

Sample	Box no.	Day 94 (31.01.94) Sum Aquamul	Box no	Day 118 (24.02.94) Sum Aquamul	Box no. / Sample no.	Day 145 (23.03.94) Sum Aquamul
AQUM	3	4530	3	3580	3-1	4440
	8	4720	8	3820	3-2	4580
					3-3	3720
					8-1	3730
					8-2	3290
					8-3	3120
mean		**4625**		**3700**		**3813**

Day 0 0-1 cm sediment layer was collected.
On the remaining days sediment layer of 0-2 cm was collected.

Figure 2.1

Gas chromatograms of Aquamul sediment extracts from day 0, day 31, and day 61 together with a gas chromatogram of standard Aquamul ether (mixture of Aquamul B II and Aquamul B drilling fluid). Dioctyl ether is added as internal standard.

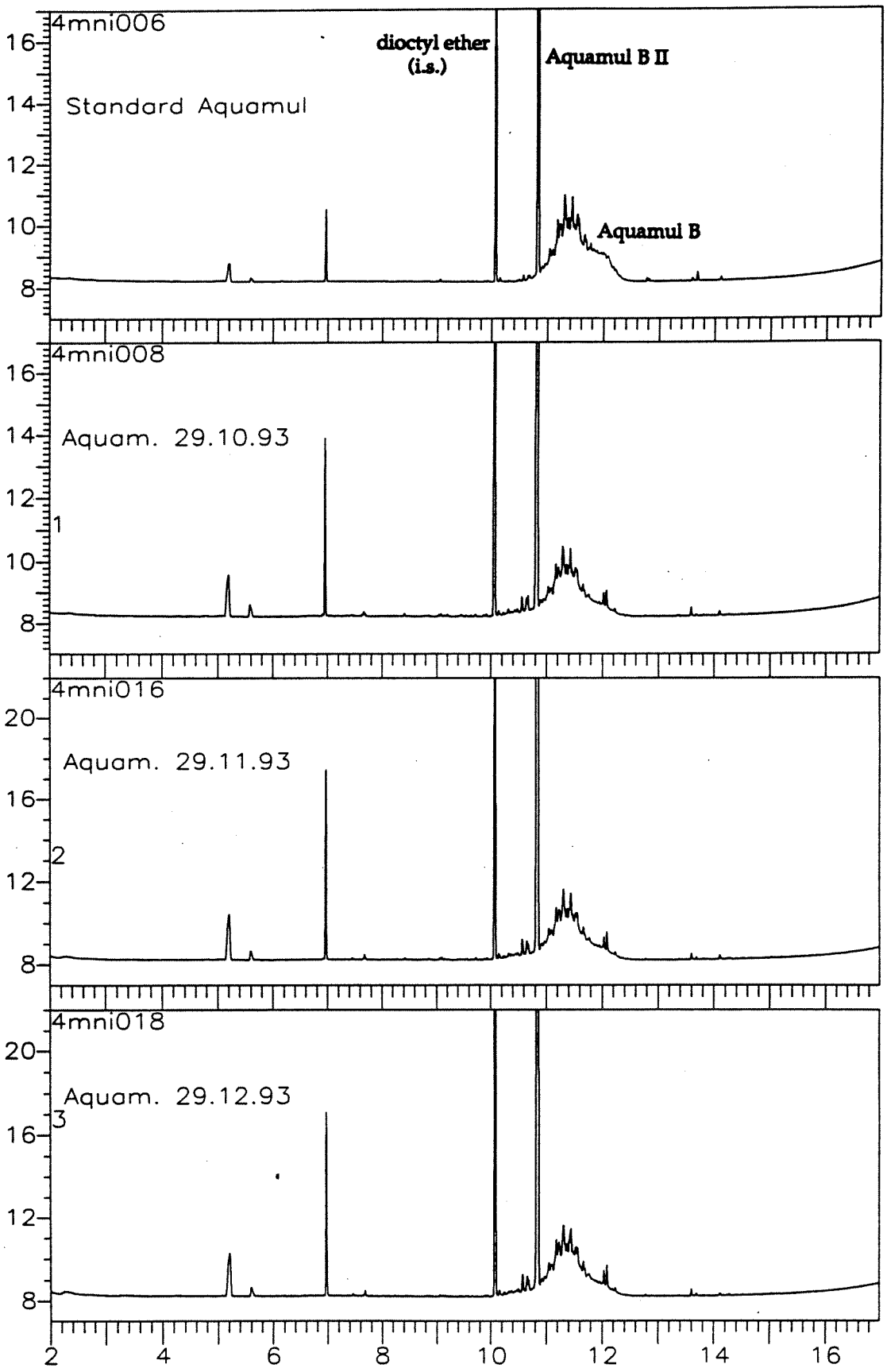
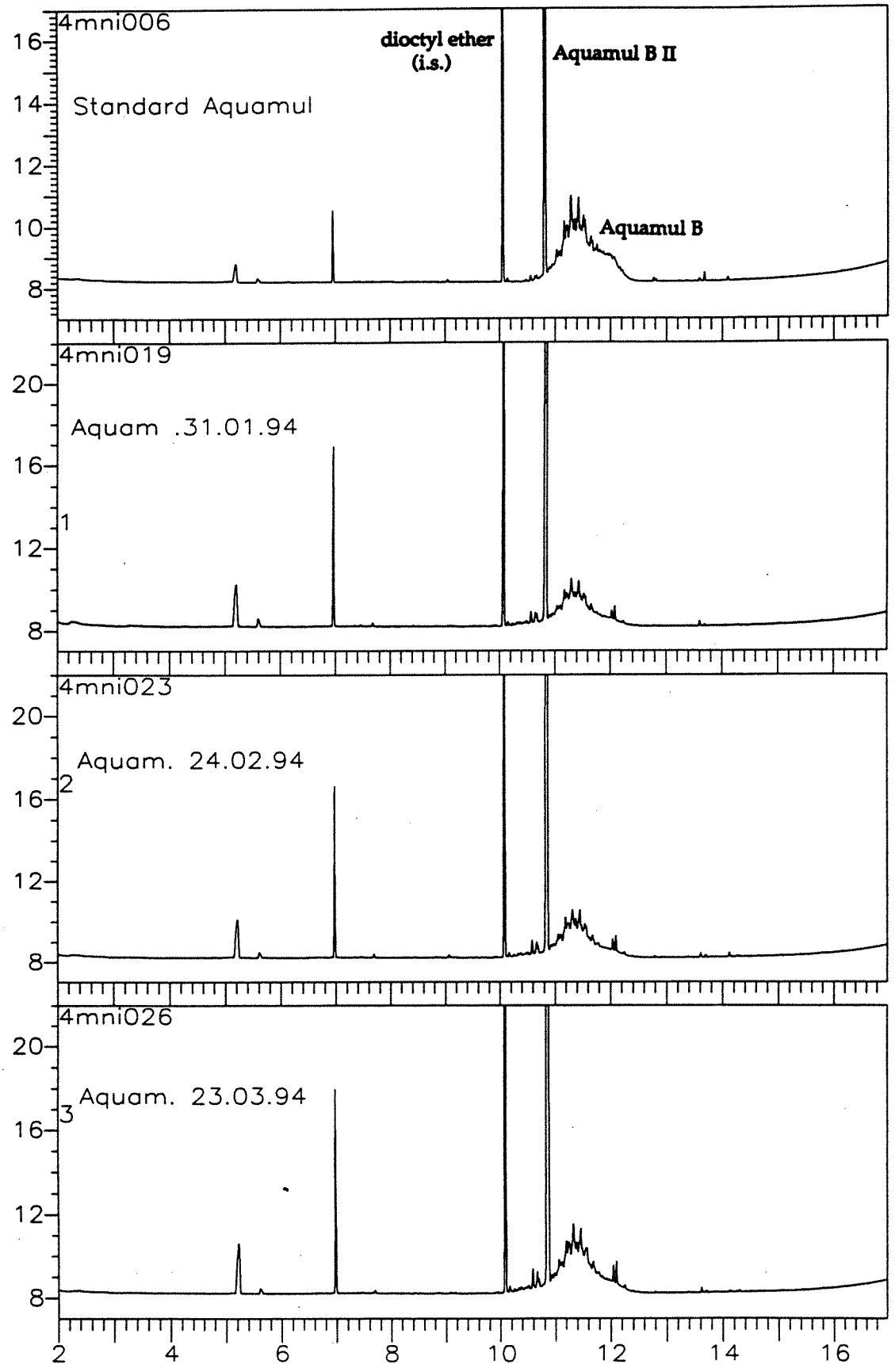


Figure 2.2

Gas chromatograms of Aquamul sediment extracts from day 94, day 118, and day 145 together with a gas chromatogram of standard Aquamul ether (mixture of Aquamul B II and Aquamul B drilling fluid). Dioctyl ether is added as internal standard.



3. MINERAL OIL

DESCRIPTION OF THE ANALYTICAL PROCEDURE, QUALITY ASSURANCE PROGRAMME AND THE RESULTS OF THE HYDROCARBON ANALYSES

3.1 ANALYTICAL PROCEDURE

3.1.1 Work up procedure

The chemical analysis includes determination of the total hydrocarbon content in sediments samples. An account of the quality assurance programme for the chemical analyses is given below.

The sediment work-up procedure is based on a method which has been used since 1978 both at the Institute for Marine Research in Bergen and SI, and which was later recommended by the Intergovernmental Oceanographic Comission ("The Determination of Petroleum Hydrocarbons in Sediments, UNESCO 1982).

Wet sediment samples weighing 15-20 g were homogenized. The samples were thereafter saponified in 80 ml of 0.5 M methanolic KOH under reflux for 2 hours. The mixture was filtered under suction and washed with 50 ml methanol and finally extracted twice with dichloromethane. The combined dichloromethane extracts were washed with water and dried over Na_2SO_4. The sediment extracts were then evaporated to near dryness and re-dissolved in hexane. Polar components were removed by chromatographing on Bond-Elut silica columns (Analytichem International) and the eluate was concentrated and analysed for total hydrocarbon content by Gas Chromatography (GC).

An aliquote of the wet homogenized sediment was weighed out for determination of the dry weight and dried for 48 hours at 105°C

3.1.2 Determination of total hydrocarbon content (THC)

Total hydrocarbon levels were determined by gas chromatography (GC). Quantitation of THC was carried out by measuring the flame ionization detector response within the boiling range of n-C_{10} alkane to n-C_{40} alkane. The area was compared to the corresponding response of known amounts of the drilling mud base oil BP 83 HF. Integrated areas were corrected for background levels from solvents (procedural blanks).

The GC analyses were carried out under the following conditions:

Gas chromatograph	: HP 5880 with HP auto sampler Mod 7673B1
Column	: 12.5 m x 0.20 mm i.d., fused silica, cross-linked with dimethyl silicone
Temperatures	
Column	: 50°C (3 min) - 20°C/min - 350°C (10 min)
Injector	: 280°C
Detector	: 350°C
Carrier gas	: Hydrogen
Injection volume	: 1 µl
Data system	: Turbochrom 3

Typical gas chromatograms are shown in Figure 3.1-3.2

3.2 QUALITY ASSURANCE PROGRAMME

3.2.1. Preparation of samples and equipment

Trace analysis requires control of the background levels of hydrocarbons in both chemicals and equipment. All chemicals are therefore purified prior to use. In addition, the total analytical procedure is checked at regular intervals by routinely analyzing procedural blanks.

HPLC grade dichloromethane, hexane and methanol are used. All equipment is rinsed with dichloromethane and heated at 600°C over night. Cleaned equipment is kept wrapped in aluminium foil.

The instruments are regularly calibrated using appropriate standards and instrument performance is checked at regular intervals.

3.2.2. Accuracy

The accuracy of the THC method employed in this study was checked by spiking non-contaminated sediments with known amounts of a drilling mud base oil. An average recovery of 80.5% was obtained after work up and analysis of three sediment samples spiked with 1000 ppm oil.

3.2.3 Reproducibility

The reproducibility of the analytical procedure was determined by analysis of sediment samples spiked with known amounts of oil. From the three sediments spiked with 1000 ppm drilling mud base oil a relative standard deviation of 3.3% was obtained for the THC determination.

3.2.4 Quantitation limit

In these experiments the quantitation limit for mineral oil was set to 30 mg/ kg dry sediment.

3.3 MINERAL OIL - RESULTS AND DISCUSSION

3.3.1 Total hydrocarbon content in sediments from the mineral oil mud trays

The results from the analyses of the total hydrocarbon content in sediment samples collected in the two mineral oil trays are given in Table 3.1.

At intervals (day 0, 31, 61, 94, 118 and 145) samples were taken for total hydrocarbon analyses. The samples were collected at random. At day 0 and day 145 three replicate samples were taken from each of the two mineral oil trays. At day 31 61, 94 and day 118 one sample was taken from each of the two mineral oil trays.

On day 0 a sediment layer of 0-1 cm was collected of all the samples. On the remaining sampling days a sediment layer of 0-2 cm was collected. This has to be taken into consideration during the interpretation of the results because sampling a thicker sediment layer will result in a dilution of the mineral oil in the sediment samples.

Figure 3.1 and 3.2 show a gas chromatogram of a standard mineral oil 83 HF together with gas chromatograms of mineral oil sediments extracts from day 0, day 31, day 61, day 94, day 118 and day 145.

3.3.2 Discussion

The results from the analysis of mineral oil listed in Table 3.1 indicate that a reduction in the mineral oil, content has taken place from day 31 to day 145 (0-2 cm sediment layer is sampled in both cases).

Looking at the gas chromatogram of the sediment extract from day 145 (23.03.94) the hydrocarbon pattern indicates that a biodegradation of the mineral oil has started. Biodegradation primarily removes the straight-chain hydrocarbons, and in the later stages the branched saturated hydrocarbons. In the gas chromatograms from day 145 the n-alkanes are reduced compared to the branched hydrocarbons pristane and phytane.

Statistically treatment of the mineral oil results showed that at a 95% confidence level there is a signinficant reduction of mineral oil from day 0 to day 145. (Telefax from Morten Schaanning, NIVA dated 11.05.94).

Table 3.1

TOTAL HYDROCARBON CONTENT IN SEDIMENTS (mg/kg dry sediment)

Sample	Box no. / Sample no.	Day 0 (29.10.93)	Box no	Day 31 (29.11.93)	Box no	Day 61 (29.12.93)
MOM	1-1	2080	1	798	1	1150
	1-2	1880	6	1120	6	999
	1-3	2000				
	6-1	2100				
	6-2	2640				
	6-3	2810				
mean		**2252**		**959**		**1075**

Table 3.1 (continued)

Sample	Box no.	Day 94 (31.01.94)	Box no	Day 118 (24.02.94)	Box no. / Sample no.	Day 145 (23.03.94)
MOM	1	1090	1	805	1-1	900
	6	184 *	6	925	1-2	771
					1-3	640
					6-1	789
					6-2	853
					6-3	602
mean		**552**		**865**		**759**

Day 0 0-1 cm sediment layer was collected.
On the remaining days sediment layer of 0-2 cm was collected.

* May be due to patchy distribution of the MOM on the sediment surface.

Figure 3.1

Gas chromatograms of mineral oil sediment extracts from day 0, day 31, and day 61 together with a gas chromatogram of standard oil 83 HF.

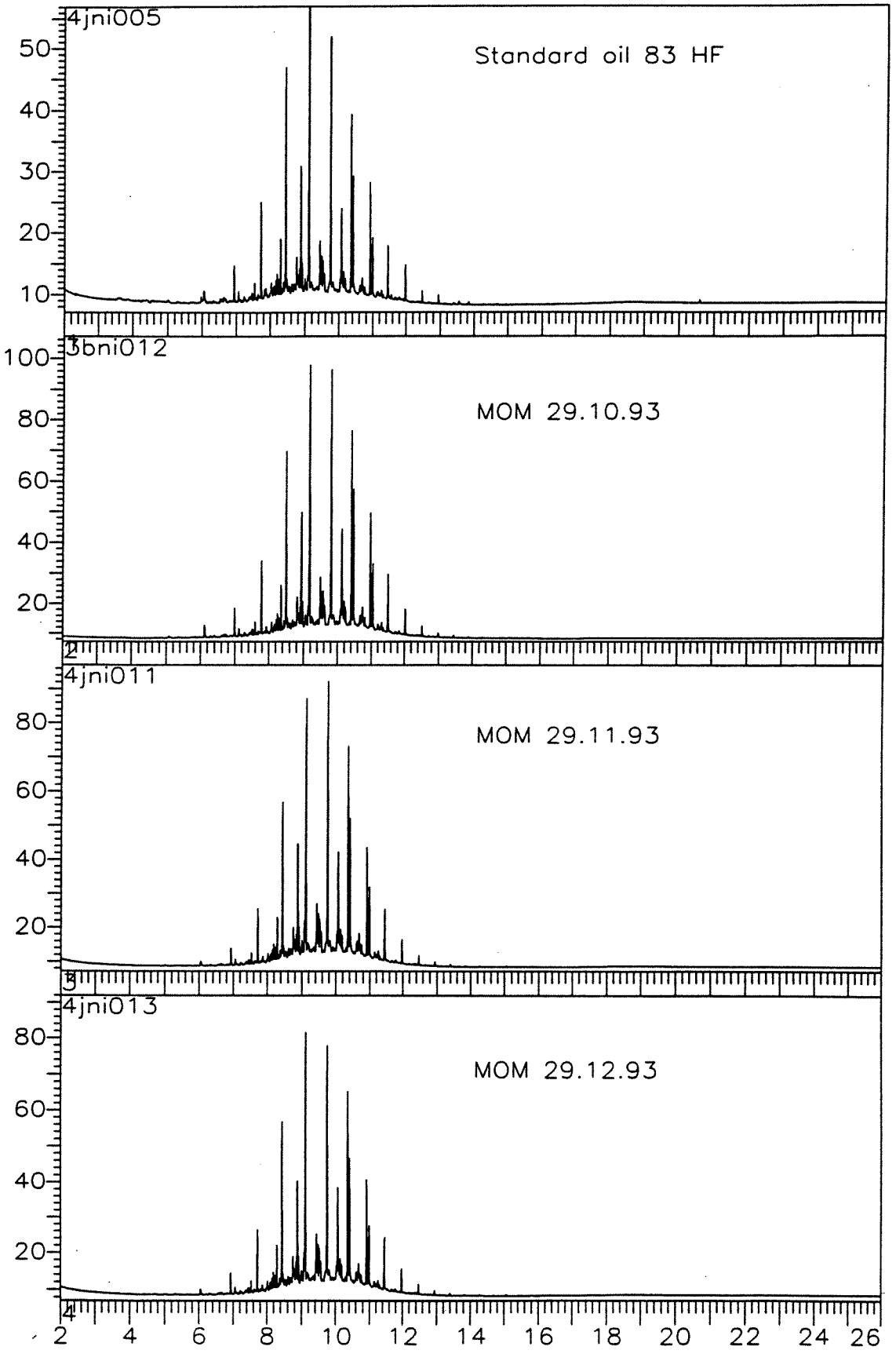
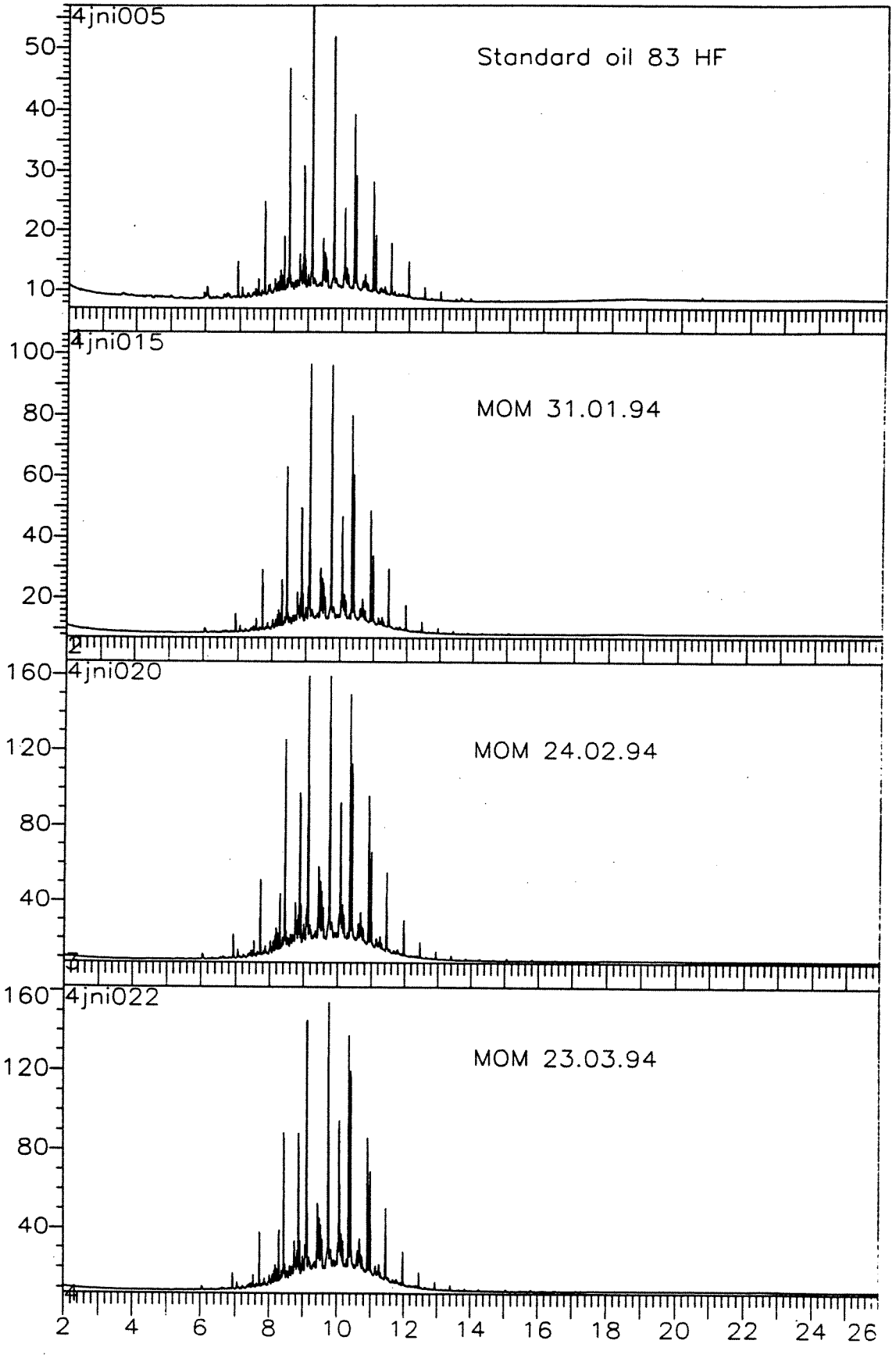


Figure 3.2

Gas chromatograms of mineral oil sediment extracts from day 94, day 118, and day 145 together with a gas chromatogram of standard oil 83 HF.



4. PETROFREE ESTERS

DESCRIPTION OF THE ANALYTICAL PROCEDURE, QUALITY ASSURANCE PROGRAMME AND THE RESULTS OF THE PETROFREE ESTER ANALYSES

4.1 ANALYTICAL PROCEDURE

4.1.1 Identity of Petrofree

A sample of the Petrofree ester was available from Baroid. Previously the chemical has been analysed at SI by computerized gas chromatography - mass spectrometry. The chemical is a mixture 5 homologous fatty acid esters. Their names and abbreviations are given below together with the internal standard used in the analyses.

1. 2-etylhexyl octanoate	(C_8 : C_8)
2. 2-etylhexyl decanoate	(C_{10} : C_8)
3. 2-etylhexyl dodecanoate	(C_{12} : C_8)
4. 2-etylhexyl tetradecanoate	(C_{14} : C_8)
5. 2-etylhexyl hexadecanoate	(C_{16} : C_8)
etyl stearate	(IS)

4.1.2. Work up procedure

The chemical analyses involve determination of the Petrofree ester content in sediment samples. An account of the quality assurance programme for the chemical analyses is given below.

The sediment workup procedure is based on a Soxhlet extraction method applied at the Herriot-Watt University in Scotland (Herriot-Watt, Statfjord environmental Survey, June 1984, Report to Mobil Exploration Norway Inc.).

Wet sediment samples weighing 15-20 g were homogenized and placed in a Soxhlet tube. Internal standard, ethyl stearate was added. The tube was refluxed with 70 ml methanol for 2.5 h. The methanol was then decanted and the sample was further extracted by refluxing with 80 ml dichloromethane over night (17 h.). The methanol extract was diluted with 70 ml of water and extracted twice with dichloromethane (40+35 ml). The dichloromethane extracts were combined, washed with 2x50 ml of water and dried over sodium sulfate. The sediment extracts were then evaporated to a suitable volume and analysed by GC for fatty acid esters. An aliquote of the wet and homogenized sediment was weighed out for determination of the dry weight and dried for 48 hours at 105°C.

4.1.3. Determination of Petrofree ester content

The Petrofree ester is a mixture of five homologous fatty acid esters. The main component is 2-ethylhexyl dodecanoate. Petrofree ester levels were determined by gas chromatography (GC). Quantitation was carried out by measuring the flame ionization detector response of the main component 2-ethylhexyl dodecanoate. The area was compared to the corresponding response of known amounts of the internal standard, ethyl stearate. The GC analyses were carried out under the following conditions:

Gas chromatograph	: HP 5880 with HP auto sampler Mod 7673B1
Column	:12.5 m x 0.20 mm i.d., fused silica, cross-linked with dimethyl silicone
Temperatures	
Column	: 50°C (3 min) - 20°C/min - 350°C (10 min)
Injector	: 280°C
Detector	: 350°C
Carrier gas	: Hydrogen
Injection volume	: 1 µl
Datan system	: Turbochrom 3

Typical gas chromatograms are shown in Figure 4.1 - 4.2.

4.2 QUALITY ASSURANSE PROGRAMME

4.2.1. Preparation of samples and equipment

Trace analysis requires control of the background levels of hydrocarbons and esters in both chemicals and equipment. All chemicals are therefore purified prior to use. In addition, the total analytical procedure is checked at regular intervals by routinely analyzing procedural blanks.

HPLC grade dichloromethane, hexane and methanol are used. The Soxhlet tubes are precleaned by extraction with methanol and dichloromethane for 2 h. All equipment is rinsed with dichloromethane and heated at 600°C over night. Cleaned equipment is kept wrapped in aluminium foil.

The instruments are regularly calibrated using appropriate standards and instrument performance is checked at regular intervals.

4.2.2. Accuracy

The absolute recovery of the Petrofree compounds and the ethyl stearate (internal standard) has previously been examined (ref: SI report 900914 Oct. 1990). An additional standard (d_{10}-pyrene) was added after sample preparation but prior to GC/MS analysis. For three replicate "clean" sediments spiked with 50 mg (1200 ppm)

of Petrofree ester an absolute recovery of 84 % was found. Correspondingly, the absolute recovery of ethyl stearate was 79 %. These results shoved a slightly better recovery of the Petrofree ester than the internal standard. Thus the Petrofree ester quantitation by use of the internal standard gave a value of 105 % of the added amount.

4.2.3. Reproducibility

The reproducibility of the analytical procedures has previously been examined by analysis of sediment samples spiked with known amounts of Petrofree ester. From three replicate Petrofree contaminated samples a relative standard deviation of 1.1% was obtained.

The reproducibility of the instrumental analysis (GC) of Petrofree ester was determined by analysing a standard solution consisting of Petrofree ester and the internal standard. The Petrofree standard was analysed together with the 20 samples. Three Petrofree standards were analysed followed by the 6 samples from day 0. Two Petrofree standards were analysed after every six sample. This gave a total of nine Petrofree standards. The relative standard deviation between the 9 analysed Petrofree standards was 2.4%.

4.2.4 Quantitation limit

In these experiments the quantitation limit for Petrofree ester was set to 2 mg/kg dry sediment.

4.3 PETROFREE ESTER - RESULTS AND DISCUSSION

4.3.1. Content of Petrofree ester in sediments from the Petrofree trays.

The results from the analyses of the content of Petrofree ester in sediment samples collected in the Petrofree ester tray are given in Table 4.1.

At intervals (day 0, 31, 61, 94, 118 and 145) samples were taken for Petrofree ester analyses. The samples were collected at random. At day 0 and day 145 three replicate samples were taken from each of the two Petrofree ester trays. At day 31 61, 94 and day 118 one sample was taken from each of the two Petrofree ester trays.

On day 0 a sediment layer of 0-1 cm was collected of all the samples. On the remaining sampling days a sediment layer of 0-2 cm was collected. This has to be taken into consideration during the interpretation of the results because sampling a thicker sediment layer will result in a dilution of the Petrofree ester in the sediment samples.

Figure 4.1 and 4.2 show a gas chromatogram of Petrofree ester standard spiked with ethyl stearate (internal standard) together with gas chromatograms of Aquamul sediments extracts from day 0, day 31, day 61, day 94, day 118 and day 145.

4.3.2 Discussion

The results from the analysis of Petrofree ester listed in Table 4.1 show a pronounced reduction in the Petrofree ester content from day 31 to day 145. Between day 31 and day 94 the Petrofree ester content in the sediment is reduced with a factor of ten (0-2 cm sediment layer is sampled in all cases).

The gas chromatograms in Figure 4.1 and Figure 4.2 clearly show the difference in the ester pattern between day 0 and day 145.

Statistically treatment of the Petrofree ester results showed that at a 95% confidence level there is a significant reduction of Petrofree ester from day 0 to day 145. (Telefax from Morten Schaanning, NIVA dated 11.05.94).

Table 4.1

CONTENT OF PETROFREE ESTER IN SEDIMENTS (mg/ kg dry sediment)

Sample	Box no. / Sample no.	Day 0 (29.10.93)	Box no	Day 31 (29.11.93)	Box no	Day 61 (29.12.93)
PFE	5-1	4310	5	591	5	160
	5-2	3640	4	683	4	261
	5-3	3780				
	4-1	4310				
	4-2	3790				
	4-3	3410				
mean		**3873**		**637**		**211**

Table 4.1 (continued)

Sample	Box no.	Day 94 (31.01.94)	Box no	Day 118 (24.02.94)	Box no. / Sample no.	Day 145 (23.03.94)
PFE	5	64	5	16	5-1	15
	4	57	4	19	5-2	11
					5-3	11
					4-1	13
					4-2	14
					4-3	14
mean		**61**		**18**		**13**

Day 0 0-1 cm sediment layer was collected.
On the remaining days sediment layer of 0-2 cm was collected.

Figure 4.1

Gas chromatograms of Petrofree sediment extracts from day 0, day 31, and day 61 together with a gas chromatogram of standard Petrofree ester. Etyl stearate is added as internal standard.

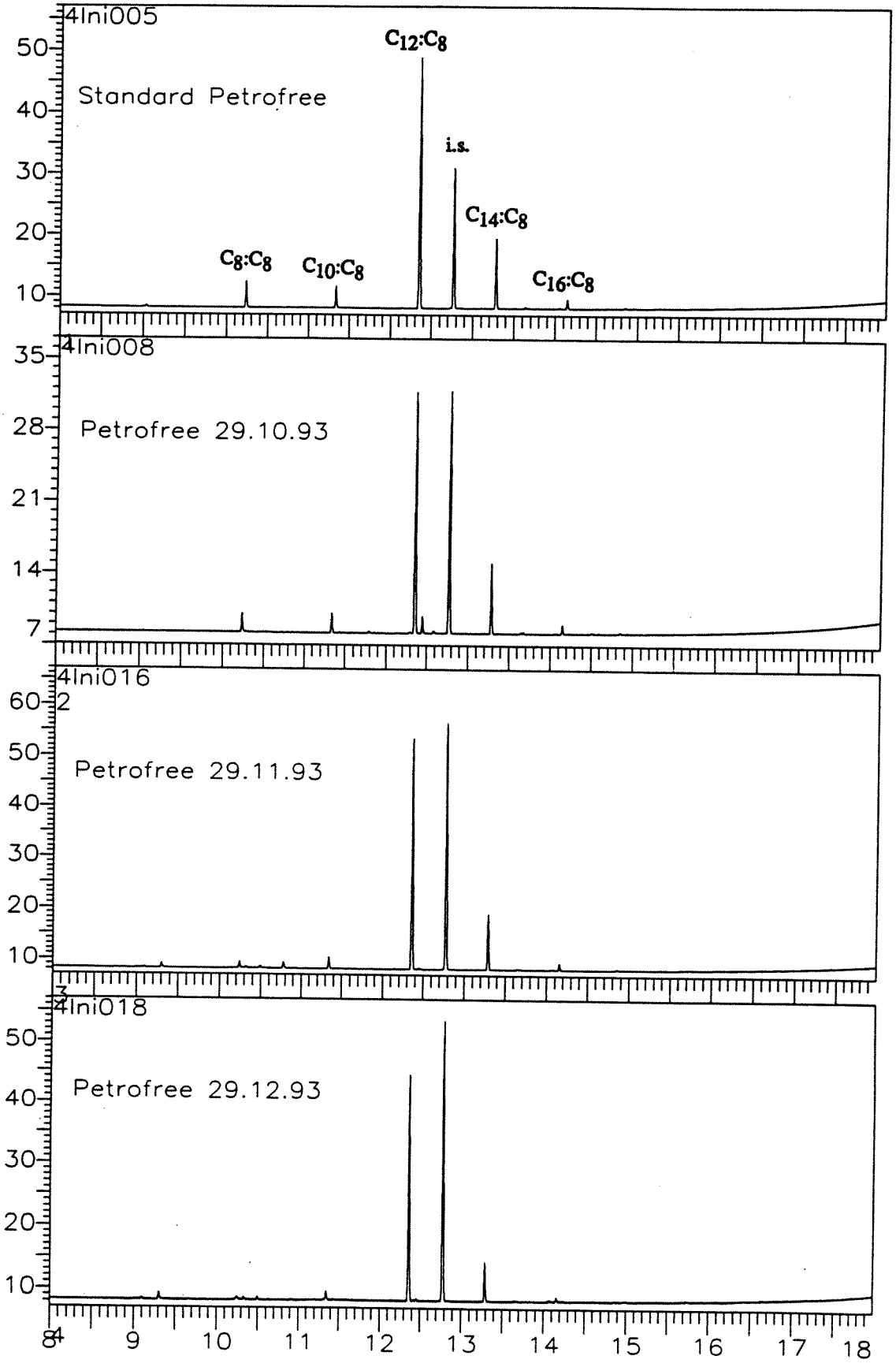
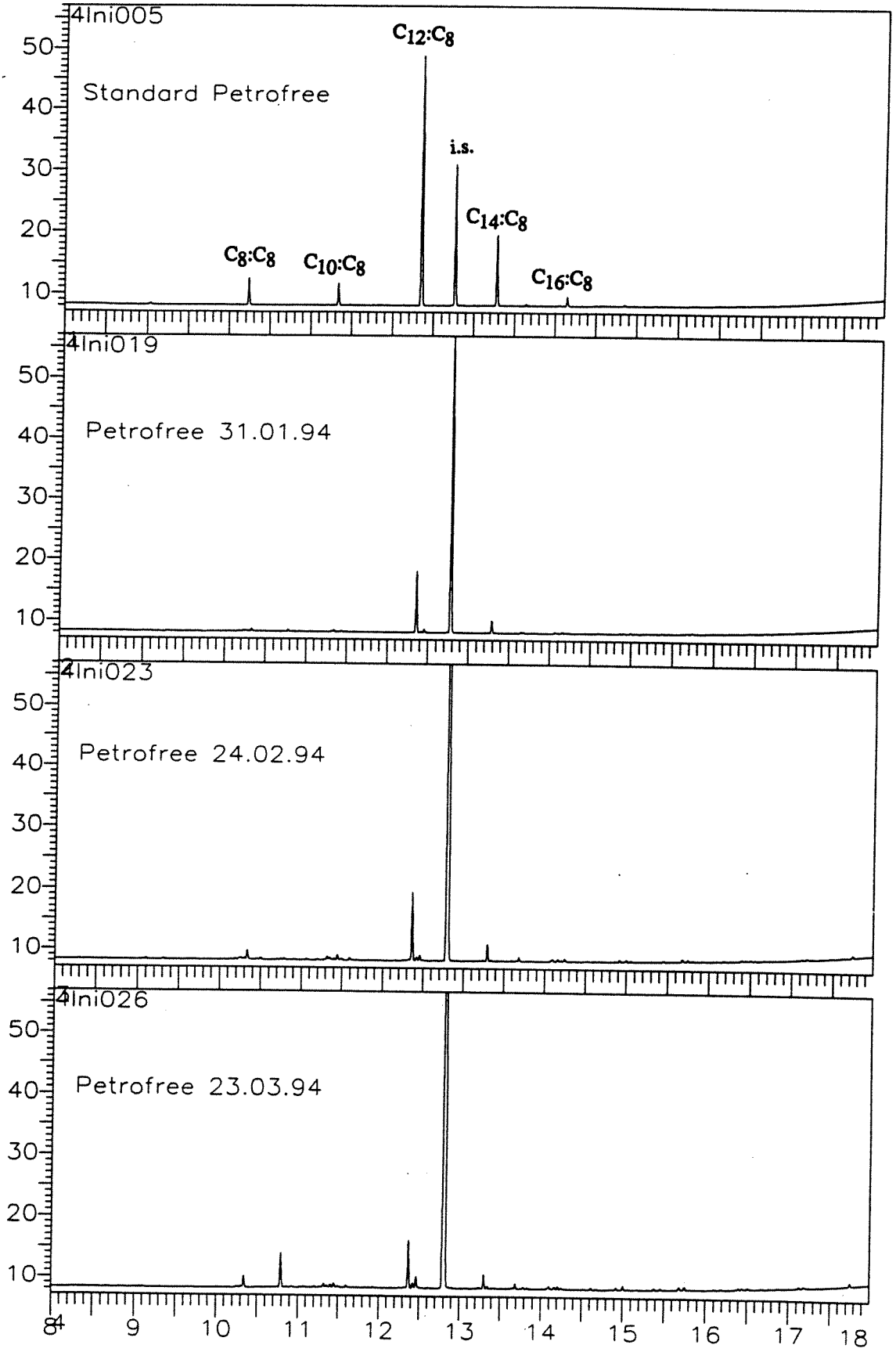
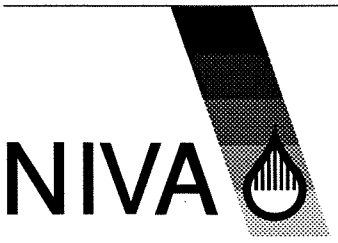


Figure 4.2

Gas chromatograms of Petrofree sediment extracts from day 94, day 118, and day 145 together with a gas chromatogram of standard Petrofree ester. Etyl stearate is added as internal standard.





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