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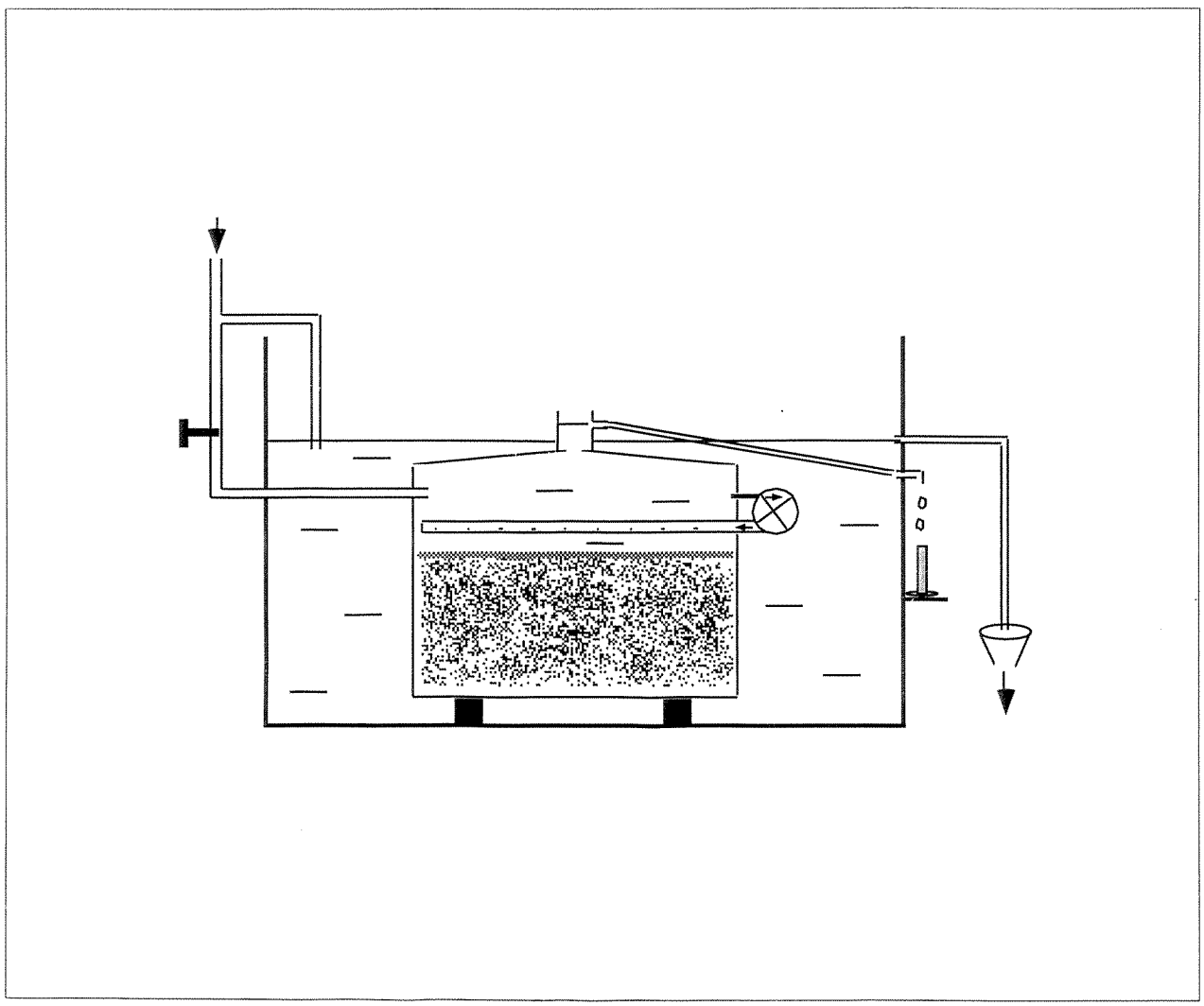
Environmental Fate of Synthetic Drilling Fluids from Offshore Drilling Operations

An Experimental Study of an Olefin-, Ether- and Ester-Based Mud System on Cuttings Deposited in Benthic Chambers



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Abstract:

Synthetic drilling fluids have replaced much of the mineral oil previously used in mud systems for off-shore drilling operations. The chemicals are entered into the North Sea environment attached to bore hole cuttings, which are deposited on the seabed not far from the discharge sites. After deposition, erosion may occur by biodegradation, bioturbation, resuspension and release to the watermass of dissolved chemicals or metabolites. In the present investigation, aliquots of control sediment and three types of cuttings were deposited in duplicate benthic chambers. During an experimental period of 161 days, the loss of drilling fluids from the sediments as well as the change of the ratio between drilling fluid and barium was measured. The mineralisation of drilling fluid carbon to CO_2 and water was calculated from oxygen consumption measurements and effects on sediment pH and redox potentials were determined at various time intervals. The results showed that Novasol II polyalfaolefins and Aquamul ethers degraded more slowly than Petrofree esters. However, as shown by strong redox potential deviations, the availability of the esters to sulphate reducing bacteria will most likely reduce the diversity of benthic communities during the degradation period.

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Environmental Fate of Synthetic Drilling Fluids from Offshore Drilling Operations

An Experimental Study of an Olefin-, Ether- and Ester-Based Mud System on Cuttings Deposited in Benthic Chambers

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Contents

Preface

The present report is written to replace NIVA-report no. 3178. The report describes the results of NIVA projects O-94066, which was performed for Saga Petroleum a.s. on request from SFT, and E-9445 which was funded by NIVA's internal research budget. The experimental work was done at NIVA Marine Research Station Solbergstrand (MFS) during the period March-September 1994. SINTEF Department of Industrial Chemistry (SI) was subcontracted to perform the chemical analyses of drilling fluids and barium. After the final report (no. 3178) had been delivered to Saga, an error in the GC-analyses of Aquamul ethers was discovered and a new subreport was prepared from SINTEF Industrial Chemistry. Because of the analytical error, the calculated Aquamul half-lives in report no. 3178 were wrong and some of the conclusions based on the comparative study of the two other drilling fluids needed modification. Meanwhile new tests have been performed, a different statistical approach has been introduced and in the process of reevaluating the entire set of observations, different phrases may have been chosen. All major changes will appear in chapters 2.3, 3.1 and 3.4 and in the summary. The major conclusions have, however, not been changed.

Oslo, March 05, 1996

Morten T. Schaanning
Project Manager

SUMMARY

Introduction and objectives of the experimental study

Synthetic drilling fluids have replaced much of the mineral oil previously used in mud systems for off-shore drilling operations. Thus, a new series of chemicals attached to bore hole cuttings, are being discharged from installations in the North Sea. Dependent on particle properties, water depth and the present current regime, some lateral transport will occur, but most of the cuttings will be deposited on the sea bed within less than about 5 km from the discharge site.

The objectives of the present investigation was to assess the environmental fate of the chemicals after deposition and certain effects on the ecosystem at the sediment-water interface. The assessment was based on a five months experiment on biodegradation of drilling fluids attached to cuttings deposited on replicate test communities. The soft bottom test communities were held in benthic chambers at the Marine Research Station Solbergstrand (MFS), which is situated by the Oslofjord south of the sill at Drøbak.

Three types of synthetic drilling fluids are currently in use. ***Ester*** and ***ether*** compounds are characterized by oxygen atoms inserted in the carbon chains. The ester bond is more easily hydrolysed than the corresponding ether bond, and previous studies have shown that biodegradation of ester base fluids on cuttings occurred at much faster rates than the biodegradation of ether base fluids. The third type of synthetic drilling fluids are based on ***olefin*** compounds. Olefins contain no oxygen atoms and biodegradation is probably dependent on an initial enzymatic cleavage of the terminal carbon-carbon bond. Previous investigations have shown that biodegradation of olefin base fluids occur at a rate comparable to ether and mineral oil base fluids.

The present test object was a new type of olefin base fluid, which is produced by *MI Drilling Fluids* by oligomerization of straight chain $C_{10}H_{20}$ α-olefins and marketed as a poly-α-olefin under the trade name *Novasol II. Novadril II* is the trade name of the corresponding mud system. GC-MS analyses showed that the Novasol II base fluid consisted of saturated hydrocarbon compounds with the chemical formula $C_{20}H_{42}$. Thus, the terminal double-bond of the olefin reactants, which might have had some environmental importance by enhancement of the initial step of biodegradation, was not found to be present in the test object[1].

The fate of the Novasol II drilling fluid on cuttings was to be compared to the fate of previously tested ester and ether base fluids on cuttings. The ester base fluid delivered from Baroid under the trade name Petrofree is a mixture of five homologous fatty acid esters, mostly 2-ethylhexyl dodecanoate (C_{12}:C_8) and 2-ethylhexyl tetradecanoate (C_{14}:C_8). The ether base fluid delivered from Anchor Drilling under the trade name Aquamul BII, is an alkyl ether with a stoichiometry corresponding to $C_{20}H_{42}O_2$. Unfortunately, the applied cuttings sample contained a mixture of 60-70% of Aquamul BII and 30-40% of a previous product, Aquamul B, which was a complex mixture of didecyl ethers.

[1]Nevertheless, in the present report the Novasol II base fluid is frequently referred to as an olefin.

Test set-up and sampling strategy

The Novadril and Aquamul cuttings were both sampled from recent drilling operations at the Snorre field. The Aquamul cuttings sample was the same as the one used in a previous test at Solbergstrand. The Petrofree cuttings sample was made available from Saga petroleum in February 1994. This sample had never been tested before, but GC-analyses showed that the peak patterns of the esters were identical to the peak pattern of the esters in the cuttings sample used in several previous tests. Concentrations of Petrofree esters and Novadril olefins determined off-shore by retort analyses, were later confirmed by the GC-analyses performed at SINTEF Industrial Chemistry. However, the reported concentration of 3.35% of ethers in the Aquamul cuttings sample was much lower than the concentration of 11.6%, observed later by the SINTEF laboratory. This error resulted in the addition of unintentionally high amounts of esters to the Aquamul chambers.

The experiment comprised eight identical, transparent acrylic chambers. Each chamber (0.5x0.5x0.4m) was filled with a 25 cm layer of sediment and a 15 cm layer of seawater. The top layer of the sediment had been recently sampled from an unpolluted location in the Oslofjord. The batch sample was thoroughly mixed before the transfer of presumably identical aliquots of sediments and inherent organisms to each chamber. Even though care was taken to avoid mortality throughout sediment transplantation and test setup, some species and individuals were probably lost during mixing and transfer processes. Priority was given to eliminate any initial difference between replicate chambers. Thus, the test communities were composed of the organisms surviving the setup procedures.

The semi-enclosed chamber water was continuously renewed with filtered sea water supplied from 60m depth in the nearby fjord. Monitoring of the quality of the water in the header tank before distribution into separate flows for each chamber, showed that throughout the experimental period, the source water was close to saturation with oxygen and the range of temperature and salinity was 6.3-9.9°C and 33.1-34.9 PSU, respectively.

On day zero, aliquots of the cuttings samples were suspended in a small volume of seawater, added to the chamber water and allowed to settle in a few mm thin layer on top of the sediment. Thus two chambers were treated with cuttings containing Novasol II olefins, two chambers were treated with cuttings containing mixed Aquamul BII and B ethers and another two chambers were treated with cuttings containing Petrofree esters. 300 g of the respective cuttings samples were added to each of the six treated chambers. A corresponding amount of non-polluted control sediment was added to each of the two remaining chambers.

During the following five months, the chambers were sampled for various purposes and parameters at various time intervals. Thus, total loss of drilling fluids was estimated from chemical analyses of drilling fluids and barium in sediment samples collected at 7-8 weeks intervals. Complete mineralisation of drilling fluid carbon to carbon dioxide was estimated from biweekly determination of the oxygen consumption in each chamber. For the purpose of exploration of new methods for additional information on sediment processes initiated by the various cuttings additions, biogeochemical fluxes of micronutrient species and carbon dioxide was determined once by the end of the experiment. Effects of the addition of cuttings were determined every 4-8 weeks by visual inspection of the sediment surfaces and *in situ* measurements of the deviations of pH and redoxpotentials from non-polluted control sediments.

Initial concentration

The objective of the initial treatment was to obtain an evenly distributed cuttings layer corresponding to approximate concentrations of drilling fluids of 5 mg·cm^{-2}. Sediment samples collected shortly after deposition of the cuttings revealed somewhat higher initial concentrations of 6.5-10.5 mg olefins·cm^{-2}, 12.2-17.6 mg ethers·cm^{-2} and 13.1-18.5 mg esters·cm^{-2} in the chambers treated with Novadril, Aquamul and Petrofree cuttings, respectively.

The high initial concentration of Aquamul ethers resulted from dose estimates performed on the basis of an erroneously low concentration of ethers in the cuttings sample (see above).

Barium recoveries of 96-155% in all chambers and recoveries of Novasol olefins and Aquamul ethers of 93-160% were concidered to be well within acceptable limits of errors likely to show up during test-setup, but was responsible for most of the excess concentration of drilling fluids in the Novadril chambers.

Recoveries of the Petrofree ester of 189-266%, did, however, reveal the presence of a more serious error in set-up procedures. This error may have resulted from fractionation of esters in the cuttings sample during subsampling for addition and chemical analyses. Thus initial overloading of esters as well as ethers had most likely resulted from various inhomogeneities in cuttings samples. Thus, in future investigations steps should be taken to avoid possible fractionation and inhomogeneities off-shore as well as in our own laboratory.

Loss of drilling fluids and barium

The loss of drilling fluids from the sediments was assumed to follow first order reaction kinetics ($C = C_0 \cdot 10^{-kt}$). For the 165 days experimental period, exponential regression analyses, showed significant decrease ($p<0.05$) of the respective drilling fluids in each one of the four chambers treated with Novadril olefins and Petrofree esters. Significant decrease of the Aquamul ethers was found only after pooling the data from both chambers.

Half-lives (τ) calculated from the curve equations ($\tau = k/\log 2$) were 83 days for the Petrofree ester, 207 days for the Novasol II olefins and 254 days for the Aquamul ethers. The corresponding 95% confidence intervals were 61-133 days for the ester, 168-267 days for the olefins and 143-1162 days for the ethers. The latter revealed the rather poor fit of the ether data to the regression model (correlation coefficient (r) of 0.66-0.69). In previous (and later) studies half-lives close to 20 days have been found for Petrofree esters in chambers treated with ca 5 mgDF·cm^{-2}. The longer half-life found in the present test was most probably a result of the higher initial concentration of esters.

During the experimental period, processes such as bioturbation, resuspension and sampling activities may provide some redistribution of cuttings particles to locations beyond the sampled 0-2 cm sediment layer. If such loss applies to barium as well as drilling fluids, the ratio between the concentrations of barium and drilling fluids should not be changed. Other processes such as biodegradation will, however, remove drilling fluids and leave barium behind in the sediment. Thus, the DF:Ba ratio may be used to differentiate between processes removing cuttings particles and processes removing the drilling fluids only. Assuming that dissolution of the hydrofobic drilling fluids is small and that non-biological degradation is a marginal process in this environment, biodegradation is likely to be the major process causing a change in the DF:Ba ratio. Furthermore, the DF:Ba ratio should not be affected by sampling errors resulting from patchy distribution of cuttings particles.

Half-lives calculated from the decrease of the DF:Ba concentration ratios were 92 days for the Petrofree ester and 217 days for the Novasol II olefins. This was not much different from the halflives calculated from the concentration data and showed that the loss of these two drilling fluids via resuspension, sampling and bioturbation was small.

For the Aquamul treatments, the correlation coefficients (r) of 0.87-0.98 for the ether:Ba ratios showed better fits to the exponential model than the concentration data. The calculated half-life of 387 days was much longer than the half-life of 254 days calculated from the concentration data, but the entire confidence interval of 293-581 days was within the confidence interval of the concentration data (143-1162 days). Thus, as compared to esters and olefins, it could not be concluded that a larger fraction of ethers were lost via particle relocation.

Evaluation of the rate of loss of Aquamul ethers were further hampered by a sampling problem which appeared to apply to freshly deposited Aquamul cuttings and which resulted in underestimated concentrations of both barium and ethers in samples collected few days after deposition. Concidering all data on concentration of Aquamul ethers from the present as well as the preceding test, and rejecting all concentrations determined during the first survey after addition of the cuttings, a reasonably good fit (r=0.81) of the Aquamul concentration data was obtained with a model assuming a 64 days lag phase followed by an exponential loss with a half-life of 138 days and a confidence interval between 103 and 208 days.

The latter model gave the most rapid loss of Aquamul ethers from the sediments. In terms of total loss during the first year after deposition, this model showed up to 87% (95% upper confidence limit, r=0.81) loss of Aquamul ethers. Slow loss of down to 35% was calculated from the model derived from ether:Ba ratios (95% lower confidence, r=0.91). The corresponding loss of Petrofree esters was between 81% (ester:Ba, 95% lower confidence limit, r=0.87) and 98% (ester concentration, 95% upper confidence limit, r=0.88). No doubt, Aquamul ethers degraded more slowly than Petrofree esters, but the loss of Novasol olefins of between 45% (olefin:Ba, 95% lower confidence, r=0.94) and 78% (olefin concentration, 95% upper confidence, r=0.95) gave no evidence for concluding that the total loss of Aquamul ethers was any different from the total loss of Novasol II olefins. The DF:Ba ratios did, however, indicate that the biodegradability of the Novadril olefins were better than the biodegradability of Aquamul ethers.

Sediment oxygen consumption

3-point curve smoothing was applied on the series of biweekly determinations of the sediment oxygen consumption rates (SOC). This reduced the apparent range of SOC values, but had no significant impact on mean rates or cumulative SOC.

Thus, the rates of sediment oxygen consumption in the control chambers varied between 55 and 372 $\mu molO_2 \cdot m^{-2} \cdot h^{-1}$. No significant time trends were observed and the total oxygen consumption for the experimental period was 583 and 713 $mmolO_2 \cdot m^{-2}$ in the two replicate chambers, respectively.

In the chambers treated with Novadril and Aquamul cuttings, the difference between replicate chambers were larger than the difference between the treatments. The SOC observed in these four chambers ranged from 164 to 882 $\mu molO_2 \cdot m^{-2} \cdot h^{-1}$ and the total respiration over the experimental period was 1770 and 1935 $mmolO_2 \cdot m^{-2}$ in the two olefin treatments and 1771 and 1988 $mmolO_2 \cdot m^{-2}$ in the two ether treatments. Thus, for the entire period, oxygen consumption in sediments treated with olefin and ether base

fluids were approximately three times higher than the oxygen consumption in control sediments.

In the Petrofree chambers, SOC ranged from 388 to 2473 $\mu molO_2 \cdot m^{-2} \cdot h^{-1}$. The cumulative SOC was 4749 and 5864 $mmolO_2 \cdot m^{-2}$ in the two replicate chambers, respectively. Thus, for the entire period, oxygen consumption in sediments treated with ester base fluids were approximately eight times higher than the oxygen consumption in control sediments.

The oxygen consumption rates in the chambers treated with Petrofree esters were very high compared to the rates measured in previous tests on Petrofree cuttings. Obviously, this was a result of the higher initial concentration of the esters. If, then, the biodegradability of Novadril II olefins had been similar to the biodegradability of the Aquamul ethers, the higher initial concentration of the ethers should have given a higher consumption of oxygen in the chambers treated with Aquamul cuttings as compared to chambers treated with Novadril. The fact that this was not observed, supported the conclusion derived from the DF:Ba ratios above, that the biodegradability of Novadril II olefins was better than the biodegradability of the Aquamul ethers.

Successive stages in the biodegradation event

During the first two months a steady increase of the rate of sediment oxygen consumption was observed in all chambers treated with drilling fluids. Thus, in the Novadril and Aquamul chambers, the oxygen consumption increased from initial rates of 150-200 $\mu molO_2 \cdot m^{-2} \cdot h^{-1}$ to rates of about 500 $\mu molO_2 \cdot m^{-2} \cdot h^{-1}$ two months later. This high level (mean rate 510 $\mu molO_2 \cdot m^{-2} \cdot h^{-1}$) was maintained throughout the remaining experimental period. In the Petrofree chambers the rates increased more rapidly. A temporary level of 1000-1500 $\mu molO_2 \cdot m^{-2} \cdot h^{-1}$ was observed 50-60 days after addition of the cuttings, but unlike the Aquamul and Novadril chambers, a second period of sharply increasing rates was observed in both Petrofree chambers between day 60 and day 90. For the entire 62-161 days period, large fluctuations about a mean rate of 1750 $\mu molO_2 \cdot m^{-2} \cdot h^{-1}$was observed in the Petrofree chambers.

Thus, in all treatments evidence was found for the distinction between two different periods of the drilling fluid decomposition event. During the first two months, increasing rates of SOC was most likely the result of adaptation and growth of the decomposer communities to the respective cuttings added on day zero. In the Aquamul and Novadril chambers, the oxygen consumption rates indicated the presence of fairly stable decomposer communities. No evidence was found for a major contribution from sulphate reducers to the decomposition of Novasol II and Aquamul ethers.

In the Petrofree chambers, however, the proliferation of sulphide oxidising bacteria on the sediment surface and the decrease of the redox potentials to less than -100 mV, revealed a significant production of hydrogen sulphide from sulphate reducing bacteria. Obviously, the evolution of a predominantly anaerobe decomposer community characterised the biodegradation of the Petrofree esters.

A very high $O_2:\Sigma CO_2$ flux ratio of 3.8 was observed in one of the Petrofree chambers on day 161. In the other seven chambers the mean ratio of 0.97 ± 0.51 was consistent with the theoretical respiration ratio of 1.0. This indicated that towards the end of the degradation event, much of the oxygen consumed in sulphidic sediments may be used for oxidation of hydrogen sulphide or other reduced compounds. Thus, even though oxygen consumption rates in such cases does not correspond with the instantaneous metabolic activity in the sediment, they will reflect previously underestimated rates of sulphate respiration.

Nutrient fluxes

Nutrient fluxes determined on day 161 showed release of ammonium and uptake of nitrate in all treatments. The uptake of nitrate was significant at the 95 % level in the Aquamul and Petrofree treatments. Phosphate was released from control and Novadril treatments, but uptake was observed in Aquamul and Petrofree treatments. The only significant flux of phosphate was the uptake observed in the Petrofree treatment. Uptake of phosphate might result from bacterial uptake or adsorption on ferric iron oxides reprecipitating at the sediment water interface. A slight lowering of the redox potentials observed in the Aquamul chambers but not in the Novadril chambers, may have been sufficient to reduce ferric iron to divalent Fe^{2+} ions. This gave some support that the latter process may have been active in the Aquamul treatments as well as in the Petrofree treatment, in which redox potentials were very low.

Nutrient limitation has been claimed to reduce natural decomposition of mineral oil. The present observations of release of ammonium from all chambers, gave no evidence for any nitrogen limitation to the degradation of synthetic drilling fluids in the present sediments. The uptake of phosphate might indicate phosphate limitation in the Petrofree and Aquamul chambers, but as shown in the above paragraph, other explanations were possible.

The rate of nitrate consumption was roughly proportional to the rate of oxygen consumption. If the entire nitrate consumption was used for oxidation of drilling fluid carbon, decomposition via denitrification may have accounted for no more than 5% of the decomposition estimated from oxygen consumption.

Effects of the degradation of drilling fluids

Effects on the sediment environment were recorded as visual effects on the sediment surface and pH and redox potentials determined at 5, 15 and 25 mm depth in the sediments.

Thus on day 2, a few dead individuals of brittle stars were found in both Aquamul chambers, but in neither of the other chambers. On day 62, dead brittle stars were observed shrouded in the bacterial film developing on the sediment surface in the ester chambers. The development of the bacterial film had been preceded by the appearance of red and yellow patches on the sediment surface. After day 111, the sediment surface of the Petrofree chambers appeared completely black with some white patches resulting from precipitated elemental sulphur. Neither dead animals nor colour variations were ever observed in control or Novadril chambers.

Anomalous high pH values were observed in the Aquamul chambers on day 2. Similar anomalies have been observed in several previous studies and result from alkaline mineral buffers added to the mud system. The observed mean pH of 8.31 at 5 mm depth, was beyond the range of natural pH variations in marine sediments and significantly higher than the range of mean values of 7.84-7.93 observed at the corresponding depth in the other chambers, controls included. The maximum values were, however, well below accepted lower limits of effects on benthic organisms.

After day 2, a moderate lowering of the pH relative to control sediments, was observed in all treatments. The maximum negative deviations of .36-.54 pH-units occurred on day 61. The largest and most frequent negative pH deviations were observed in the Petrofree treatment. The lowering of the pH in the Aquamul chambers may have been counteracted by the presence of alkaline mineral buffers in the mud system.

After addition of cuttings the redox potential in the sediments treated with ester cuttings decreased to a negative deviation relative to control sediments of 113 mV on day 28, 164 mV on day 62 and 338-344 mV on days 111 and 161. After day 2, significant negative deviations of the E_h were observed at all depths and surveys in the Petrofree treatments, i.e. on twelve out of twelve occasions.

In the Aquamul chambers, negative Eh deviations were observed at all depths and surveys after day 2. The deviations were, however, much smaller than in the Petrofree treatment. Thus, the maximum negative deviation of -76 mV was observed at 25 mm depth on day 161, and the deviations were significant at five occasions only, of the twelve groups of observations performed after day 2.

In the Novadril treatments negative deviations occurred on seven of twelve occasions after day 2. A significant positive deviation was found at one occasion and significant negative deviations on three of the twelve possible occasions. The maximum deviation of -65mV was observed at 5 mm depth on day 161. Thus, compared to the Petrofree and Aquamul treatments, significant deviations of redox potentials relative to control sediments in the Novadril treatments were smaller, less frequent and occurred in both directions.

Mass balance of the drilling fluids present on day 2

A mass balance of the drilling fluids was constructed for each separate chamber for the period 2-161 days. In the mass balance a distinction was made between:

- *Total loss* which was calculated from the difference between the initial and final concentration of drilling fluids,
- *particle loss* or *barium correction* which was calculated from the loss of barium and which either represent a real loss of drilling fluids by sampling, resuspension or burial of cuttings particles or an apparent loss resulting from sampling errors.
- *Mineralisation* was calculated from the oxygen consumption in each chamber and will represent ultimate bio-oxidation of the drilling fluids to CO_2 and water, whereas
- *biodegradation* will include mineralisation as well as any production of metabolites which emigrate from the sampled layer or escape the chemical analyses of the drilling fluid.
- *Other loss* is the mass balance deficit calculated from the difference between initial and final concentration plus specified loss items such as mineralisation and barium loss.

The mass balance showed that of the 100% present on day 2, 58-60% of the Novadril II olefins remained present in the sediment on day 161. A similar remaining fraction of 55-60% of the Aquamul ethers was found in the present test, but as much as 68-85% was found left in the sediments on day 145 in a previous test. In the present test, the remaining fraction of Petrofree esters was 17-39%, which was high compared to previous and later tests showing loss of more than 99% of added esters. The moderate removal of esters as well as the longer half-life observed in the present test was concluded to result from the higher initial concentration.

The mineralised fraction of 10-18% of the Novadril II olefins was intermediate between the Petrofree esters and the Aquamul ethers. A mineralised fraction of 7-8% of the initial concentration of Aquamul ethers was found in all four chambers investigated during the present and preceding test. In the Petrofree chambers mineralisation could account for 25-34% of the initial concentration. In a more recent test, however, as much as 80% of the Petrofree esters were mineralised during the experimental period.

Biodegradation determined as the sum of the mineralised fraction and other loss was larger in the Petrofree treatment (49-74%) as compared to the Novadril (11-43%) and Aquamul (23% in both chambers) treatments. The comparison between the biodegradation of Novadril olefins and Aquamul ethers was, however obscured by the large variability of the barium loss between the two replicate Novadril chambers, the lack of barium data from the previous test on Aquamul ethers and the inconsistency between the remaining fraction of Aquamul ethers in the two tests.

Probably, the production of partly degraded metabolites was the most important process accounting for the other loss item in the Novadril and Aquamul treatments. In the Petrofree treatment, however, evidence was found that reduced compounds from a significant biodegradation of esters via sulphate reduction could account for a larger fraction of the other loss item in the Petrofree chambers.

Biodegradation mechanisms

From a consideration of the molecular structure, the Petrofree esters will most likely undergo a hydrolytic cleavage to yield C_{10}-C_{14} saturated fatty acids and 2-ethyl hexanol. Neither product will be determined in the ester analyses. The fact that, 49% of the total loss of esters was observed during the first 60 days of the experimental period, during which only 18% of the total consumption of oxygen was consumed, was consistent with the low oxygen requirement and the rapid loss of ester expected to occurr during enzymatic hydrolyses of the ester bond. Thus, the first 60 days was considered to represent an initial phase characterised by adaptation of the microbial community and cleavage of ester bonds.

Fatty acids are easily available to rapid β-oxidation in the mitochondria of living cells and should be fit for supporting high rates of oxygen consumption. The observation of a sharp increase of the oxygen consumption rates in the Petrofree chambers shortly after day 60, and the maintenance of high rates throughout the rest of the experimental period, indicated the evolution of a microbial community well adapted for exploitation of the ester metabolites. The simultaneous decline of the redox potential to very low values (<-100mV) showed that sulphate reducers were an important component of this community.

Reproducible patterns of initial periods of about 60 days of slowly increasing rates of oxygen consumption, followed by a level of about 400 $\mu mol \cdot m^{-2} \cdot h^{-1}$ (in excess of the oxygen consumption rates observed in control chambers), which was maintained throughout the remaining experimental period, were observed in the present and previous test on Aquamul ethers and Novadril II olefins. Thus, the oxygen consumption measurements revealed no differences which might support any different biodegradation mechanism between Aquamul ether and Novadril olefins.

In the report of the previous test, the degradation of the Aquamul ether was modelled as a two-step reaction: an initial hydrolytic cleavage of the ether bond followed by biodegradation of the metabolites. Hydrolytic cleavage of the Aquamul B and BII ethers should yield mostly branched C_4,C_8 and C_{10} alcohols. Metabolisation of alcohols are thought to occurr less easy than metabolisation of fatty acids and branching should imply a further hindrance of biodegradation.

The GC-MS analyses showed that Novasol II was a saturated and frequently branched $C_{20}H_{42}$ hydrocarbon. Thus, from the molecular structure, biodegradation of Novasol II might be expected to occurr more slowly than the biodegradation of Aquamul ethers, in which the ether bond was thought to represent a weak point available for an initial bacterial attack. Neither the mass balance consideration, nor the oxygen consumption rates gave, however, any evidence for a more rapid degradation of the ethers. On the

contrary, the mineralised fraction was slightly higher and the half-life tended to be somewhat shorter for the Novasol II olefins. Because of the rather complex structure of the Aquamul ether molecules, steric hindrance of an enzymatic attack on the Aquamul ether bond was discussed as a possible explanation to the absence of any clear differences of the biodegradation of the Novasol II olefins and the mixed Aquamul ethers.

On the other hand, ether:Ba ratios revealed a major decrease during the 60-120 days period. The fact that this occurred without any significant elevation of the oxygen consumption rates, was consistent with the low oxygen requirements of an enzymatic cleavage reaction. If the rate of ether cleavage really peaked during the 60-120 days time interval, the assumed initial lag phase of 60 days might correspond to the time required for the evolution of an ether splitting enzyme system and the following exponential decrease would primarily represent the rate of the ether cleavage reaction.

Because of the uncertainties involved, primarily in the determination of concentrations of ethers, the importance of the ether cleavage reaction as a mechanism in seabed remediation may range from negligible to a major mechanism explaining the lag phase model for the degradation of the Aquamul ether. In any case, the cleavage of the Aquamul ether was very slow compared to the cleavage of the Petrofree ester.

Conclusions

The Novasol II olefins disappeared from the sediment with a halflife close to 210 days. The data showed good fits to the exponential degradation model. Even though as much as 55-60% of the added fluid remained present in the sediment by the end of the experimental period, no evidence was found for any stagnation of the decomposition process towards the end of the experimental period. Neither macrobenthic mortality nor colour changes of the sediment surface were observed in the Novadril treatments, and pH and redox potential deviations from control sediments were smaller and less frequent than in any of the other treatments.

The degradation curves of the Aquamul BII and B ethers were characterized by more scatter than the degradation curves of the other fluids. Much of the scatter disappeared from the degradation curve of the ether:Ba ratios. The half-life calculated from the ratios were large compared to the half-life calculated from the ether concentrations. Thus, the fit to the second order reaction kinetics was questioned and a different model assuming a 60 days lag phase followed by exponential decrease was found better fit for the descripition of the Aquamul data. With this model the biodegradation rates for Aquamul ethers were not found to be significantly different from the biodegradation of the Novasol II olefins. Effects on pH and redox potentials were moderate and hydrogen sulphide was never detected in the Aquamul chambers. However, an initial pH-buffering to a level beyond the natural range of pH in marine sediments as well as some brittle star mortality was observed on day 2.

The Petrofree esters degraded more rapidly than the other drilling fluids, but accumulation of hydrogen sulphide in the pore waters may yield severe negative impacts on the benthic communities during the degradation period.

1 INTRODUCTION

Environmental concern has led to a prohibition of discharges from use of oil based mud systems (OBM) in offshore drilling operations. Consequently, low toxic water-base muds (WBM) or synthetic-base muds (SBM) are investigated by the oil industry. Superior technical performance has favoured the use of the latter, and the discharge into the North Sea of synthetic drilling fluids attached to cuttings have increased rapidly during the last few years.

Three types of synthetic drilling fluids are currently in use. ***Ester*** compounds are produced by the reaction between an acyl halide or fatty acid and an alcohol. In the environment, enzymatic cleavage of the ester bond may represent a relatively easy initial step of biodegradation. The fatty acids produced should be fit for entering the cyclic breakdown process in cell mitochondria known as β-oxidation. The central oxygen atom in ***ether*** compounds does not activate the adjacent carbon atoms to the same extent as the ester oxygen do. Biodegradation of ether compounds by enzymatic cleavage of the ether linkage has been found to occur in oxic environments, but anaerobe degradation and degradation of long chain ethers do not occur easily. In previous tests at Solbergstrand, the rate of biodegradation of ether base fluids has been found to be comparable to the rate of degradation of ***poly-α-olefin*** base fluids, both being significantly slower than the degradation of esters. The poly-α-olefins are produced by oligomerization of straight chain C_8H_{16} or $C_{10}H_{20}$ α–olefins. Most likely, the biodegradation of poly-α-olefins occur by an initial oxidation of the terminal double-bond, followed by successive oxidation up the carbon chains.

The endpoint of biodegradation of organic carbon is carbon dioxide (CO_2) or methane (CH_4). CO_2 is the terminal product of aerobic organisms as well as sulphate reducing bacteria. Thus, the large reservoir of sulphate in sea water and interstitial water will suppress methane production to deeper strata or highly enriched sediments.

After discharge the cuttings sinks through the water column. Depending on particle properties, water depth and currents, the cuttings are subdue to various lateral transport before deposition on the sea-bed. Thus, as a result of discharges of OBM cuttings, Zevenboom et. al.(1992), and others, found that the concentration of hydrocarbons (THC) exceeded back-ground levels of 0,2-5 $mg \cdot kg^{-1}$ d.wght. up to 5-12 km from drilling sites in the Norwegian sector of the North Sea. Close to the discharge sites concentrations as high as 10-100 $g \cdot kg^{-1}$ has been found. A total area of 8000 km^2 of the North Sea seabed has recently been estimated to be contaminated with elevated levels of THC (Gislasson et.al., 1993).

On the seabed, three principally different effects on the benthic ecosystems may be distinguished. One is the physical effects of smothering or burial of the pristine communities by a layer of particles. The particles and associated compounds are, however, not chemically inert. Therefore, biooxidation of organic carbon may alter the pore water environment, and toxic compounds may interact with physiological processes. All three types of effects may alter the structure of benthic communities. Removal of drilling fluids by biodegradation is thought to be the principal mechanism of seabed remediation. The present study is focused on the mass balance of drilling

fluids on cuttings added onto experimental sediments and the extent and effects of biodegradation.

It should be realised that effects may result not only from the drilling fluid itself, but from a number of components present in the mud system such as heavy metals and lime, and small amounts of biocides, corrosion inhibitors, detergents and emulsifying agents. Organic carbon components may undergo biodegradation along with the drilling fluids, and toxicity responses might show up as inhibitory effects on community respiration.

The objectives of the present study was to test biodegradation and enrichment effects of the Novadril II poly-α-olefins[2] in drill cuttings deposited on sediments maintained under environmental conditions resembling as much as possible the conditions at the North Sea seabed, and to compare the behaviour of the Novadril cuttings to other cuttings containing Petrofree® esters[3] and Aquamul® ethers[4], respectively.

The previous drilling fluid in the Novadril mud system, Novasol I, was an oligomer of the 1-octene-α-olefin, mostly (>60%) a highly branched trimer $C_{24}H_{48}$. The Novasol II is claimed to be a less branched and almost exclusively dimer product ($C_{20}H_{40}$) of the 1-decene.

[2]Novadril is a trade name for a mud system based on Novasol poly-alfa-olefin drilling fluids delivered by MI Drilling Fluids
[3]Petrofree is a trade name for a mud system based on ester drilling fluids delivered by Baroid
[4]Aquamul is a trade name for a mud system based on ether drilling fluids delivered by Anchor Drilling Fluids

2 MATERIAL AND METHODS

2.1 TEST PRINCIPLE AND SET-UP

The comparative study of the various cuttings was performed by suspending the cuttings in seawater, add the suspensions to the overlying water in replicate benthic chambers and allow the particles to settle through the sea water onto the experimental sediment. The chambers were kept submersed in dimly enlightened indoor basins. Sea water taken from 40-60 m depth in the fjord nearby was allowed to flow continuously through the chambers at rates sufficient to maintain at least 50% oxygen saturation. 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 161 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.

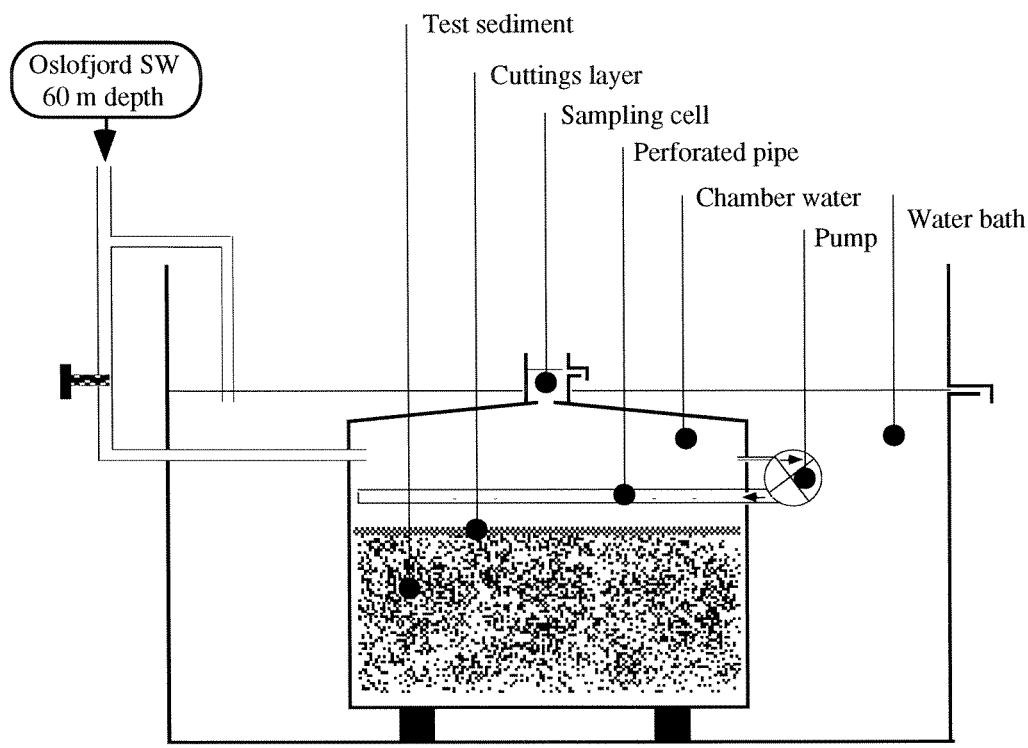

Fig. 2.1. Schematic drawing of the benthic chamber. Timercontrolled, submersed pumps generated an internal circulation by driving a flow of water through the perforated pipe. To ensure a well mixed chamber water, the pumps were activated for 15 minutes every two hours.

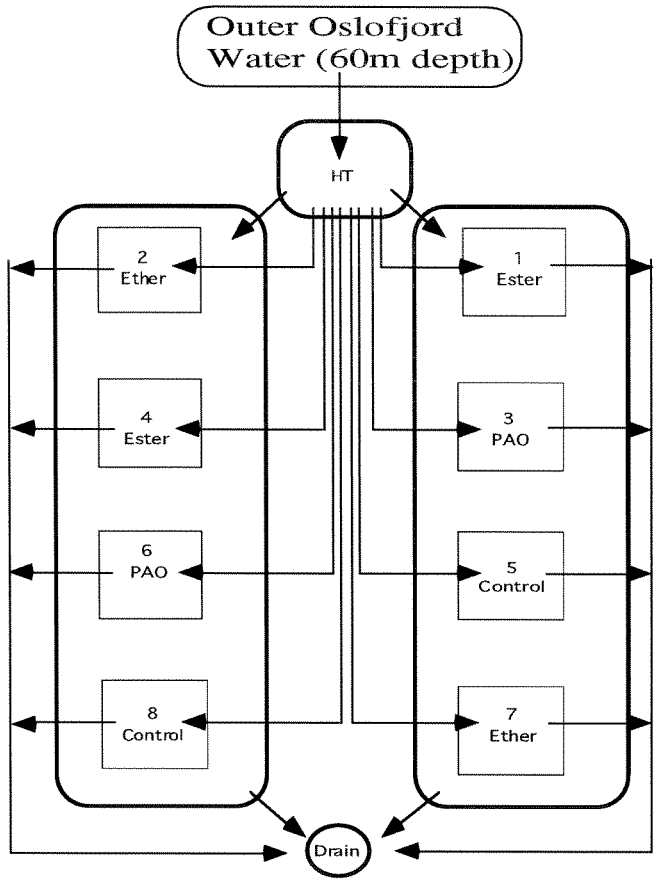

Fig. 2.2. Schematic drawing of experimental set-up and water flow. Fjord water from 60 m depth were continuously supplied to the header tank (HT). From HT, an eight channel peristaltic pump (not shown) maintained separate flows of water to each chamber. The chambers were kept submersed in two trays which were continuously flushed with overflow from the header tank.

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, Schaanning, 1994).

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 realise 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.

The design of the applied benthic chamber is shown in fig. 2.1, and the organisation of the flow system through the eight test chambers is shown in fig 2.2.

2.2 TEST ENVIRONMENT

2.2.1 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 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 33.1 and 34.9 PSU, with a mean value of 34.41 PSU. The temperature varied between 6.3 and 9.9 °C, with a mean value of 7.02 °C. The simultaneous shift to higher temperature and lower salinity at about 115 days after addition of the cuttings resulted from a temporary switch of the water inlet from 60 m to 40 m depth. The temperatures determined biweekly in the header tank agreed well with the automatic registrations.

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 0.5-3 $mg \cdot l^{-1}$ less than the concentration in the header tank. The mean oxygen concentration in the header tank is given in table 2.1 together with mean outlet oxygen concentration and flow rate through each chamber.

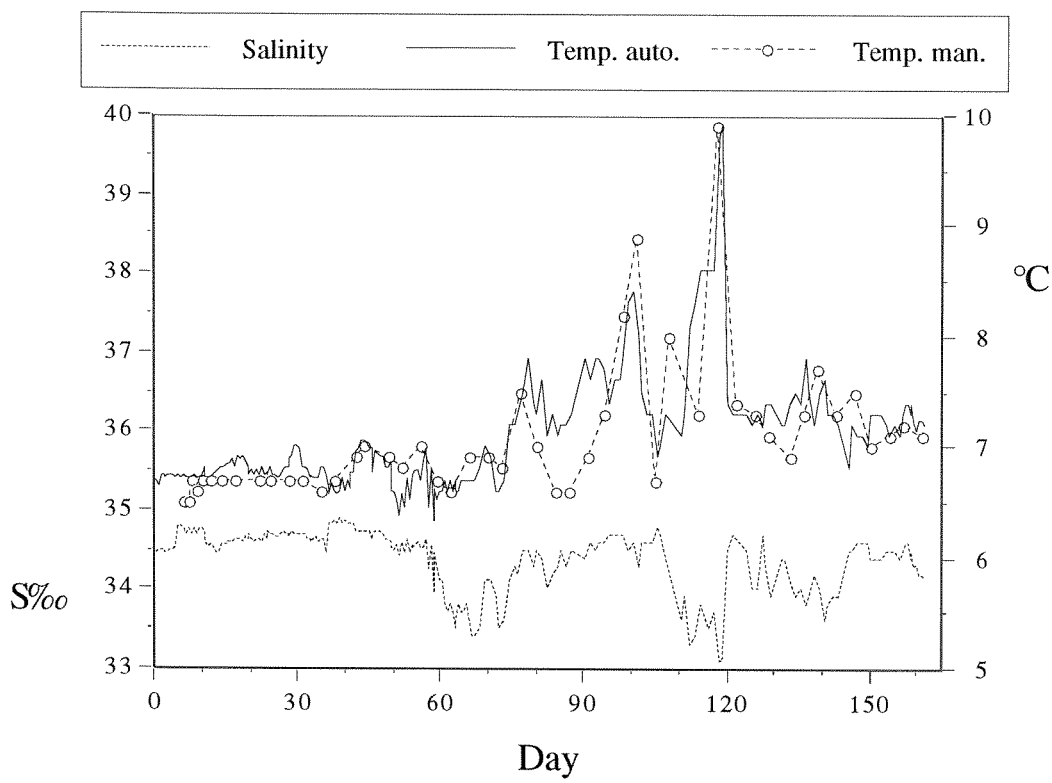

Fig. 2.3. Temperature and salinity in source water during the test period. Continuous lines show 12 hour mean values of the data collected by the monitoring programme at the Solbergstrand Research Station (Oen, pers.comm.). Open circles show independent biweekly determinations of temperatures in the header tank.

Table 2.1. Mean oxygen concentration and water flow through chambers during the test period.

	Mean	Std.dev.	Number of obs.
$[O_2]$ inlet (header tank)	7.07 $mg \cdot l^{-1}$	.63 $mg \cdot l^{-1}$	48
$[O_2]$ outlet (all chambers)	6.22 $mg \cdot l^{-1}$	.85 $mg \cdot l^{-1}$	380
Flow (all chambers)	33.6 $ml \cdot min^{-1}$	15.7 $ml \cdot min^{-1}$	377

2.2.2 Source and quality of test sediment

The applied sediment was collected 13.03.94 at Pipegrunnen south of Bevøya in the Outer Oslofjord. At Solbergstrand, the sediment was rotated for 15 minutes in a concrete mixer and aliquots of the homogeneous batch was transferred to eight benthic chambers. The chambers (48x48x37cm) were prefilled with a 15cm base layer of non-polluted 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 set-up and performance. The open chambers were then left submersed in two large trays to equilibrate with seawater from 60 m depth.

The test sediment was analysed for base line parameters such as grain size distribution, water content and organic matter (table 2.2). The grain size distribution (table 2.2) showed a rather fine grained sediment with more than 97% in the silt and clay fraction. The sediment had contents of total carbon of 1.88% and nitrogen of 0.18% and the average water content of the samples collected two days after addition of cuttings was 59.7%.

Table 2.2. Grain size distribution, water content, and the concentration of nitrogen and carbon in test sediment. Units are % of dry weight. (Analyses at NIVA-LAB).

Grain size >63 µm	2.16 %
Grain size <63 µm	97.84 %
Water	59.6 %
Nitrogen	0,18 %
Carbon (total)	1,88 %

2.3 INITIAL TREATMENT

2.3.1 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 SINTEF Industrial Chemistry in March -94 on the 34/7-A-9H cuttings sample showed that the cuttings had a much higher content of 11.6% ethers, and that the ethers in the cuttings sample was a mixture of 60% Aquamul BII ethers and 40% of the previous product Aquamul B. The concentration of ethers in sediment samples collected in the Aquamul chambers after addition of cuttings, were consistent with the latter value of 11.6%. Probably, the discrepancy between the off-shore retort analyses and the GC-analyses at SINTEF, was a result of inhomogeneities in the cuttings sample. Unfortunately, the underestimated ether concentration in the cuttings sample resulted in rather high initial concentration of drilling fluids in the Aquamul chambers.

The Petrofree cuttings were taken from a recent sample delivered by Saga petroleum in February 1994. The peak pattern of the GC-chromatograms showed that the esters in the new cuttings sample were similar to the esters in the cuttings sample used in previous tests. The concentration of esters was found to be 5.7% of the sample dry weight, which was not very different from the result of retort analyses of 4-5% reported by Saga.

The Novadril II cuttings sample was collected from Saga´s 34/7-I-IH well on 27.11.93 and delivered to NIVA from MI-Norge on 16.02.94. Two retort analyses performed by MI´s Field Service Lab showed oil contents between 6.18 % and 7.15 % (Appendix II). A subsample analysed by the GC-method at SINTEF-SI showed a total concentration of Novasol olefins of 5.6%.

2.3.2 Addition of cuttings

Cuttings were added to the experimental chambers 26.04.94. 300 g of cuttings were mixed with an appropriate volume of sea water in a steel whirl mixer. The resulting slurry was transferred to a glass bottle and added slowly into the chamber water. 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 15 cm water column. Two chambers were treated with Novadril II cuttings, two were treated with ester cuttings and two were treated with the ether cuttings. To test for possible effects of capping on oxygen consumption rates and pore water conditions, 500 g (wet wght.) of the non-polluted test sediment was added to the control chambers.

2.4 SAMPLING AND ANALYTICAL METHODS

2.4.1 Sediment samples

The time table of the sampling programme is shown in table 2.3. On the initial and final sampling days, two sediment samples for analyses of barium and drilling fluids were

Table 2.3. 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	26.04	28.04	24.05	28.06	16.08	5.10
Day	0	2	28	62	111	161
Mud added	✓					
Treated chambers						
Novadril olefins		4	0	2	2	4
Aquamul ethers		4	0	2	2	4
Petrofree esters		4	0	2	2	4
Barium		4	0	2	2	4
All chambers						
pH (9/chamber)		72	72	72	72	72
E_h (9/chamber)		72	72	72	72	72
SOC (1/chamber)		|---------- twice a week ----------|				
Header tank						
Temp. (°C)	|---------- hourly ----------|					
Salinity (S‰)	|---------- hourly ----------|					

drawn from each of the six chambers treated with cuttings. On the intermediate sampling occasions, one sediment sample was drawn from each of the treated chambers.

In addition to the samples shown in table 2.3, one of the control chambers were sampled for barium and drilling fluid analyses on days 2, 62 and 111. As a part of an internal NIVA research project, biogeochemical fluxes of carbon dioxide and nutrient species were performed on day 161.

Each sediment sample was pooled from the top 0-2 cm section cut off from five separate cores (ID≈15 mm). Each core was drawn from the grid locations shown in fig. 2.4. The grid co-ordinates were randomly chosen using the random number function of a spreadsheet program.

The total weight and the water content of the pooled sample was determined before the samples were put aside in the freezing room at Solbergstrand. After the final sample collection, the total number of 51 sediment samples were handed over to the SINTEF-Si laboratory for chemical analyses.

Analytical procedures are comprehensively described in Appendix III. Briefly, the drilling fluids were extracted from the sediment in Soxhlet tubes using methanol and dichloromethane. All extracts were analysed on gas chromatography using flame ionisation detector and quantitated by addition of known amounts of internal standards to each sample prior to extraction.

Barium was analysed on pelletised samples of the dried sediment using x-ray fluorescence.

2.4.2 Sample work-up and concentration units

The set-up of the experiment implicated that all of the cuttings were present in a few mm thin layer at the sediment-water interface. Therefore, concentrations related to sediment weight will be crucially dependent on the sediment depth at which the core-sample is cut off. Because of biofilms growing on the sediment surface or animal activities creating tracks and mounds, accurate determination of the sediment water

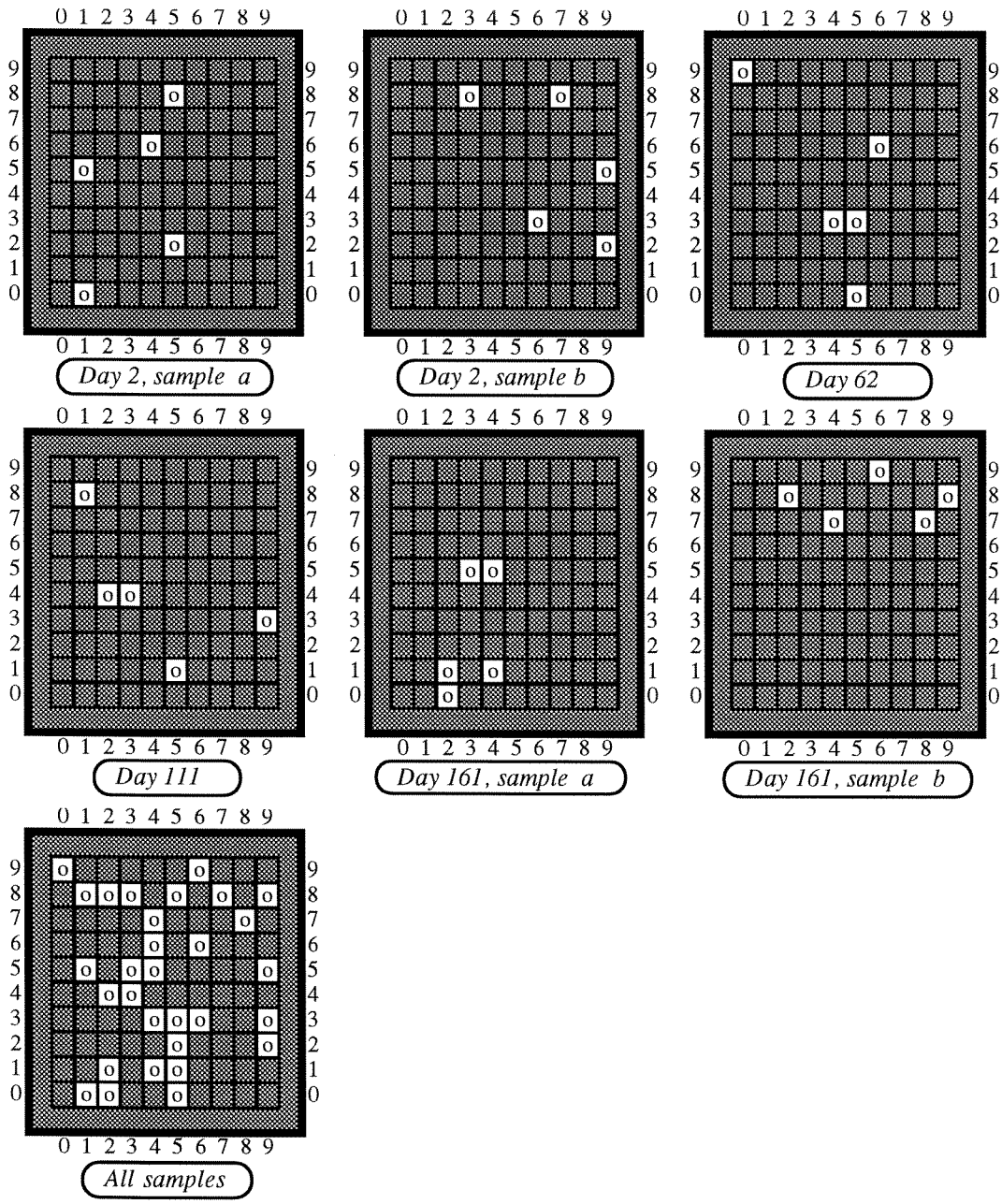

Fig. 2.4. Grid system and randomly chosen locations for each one of the five core samples pooled for one chemical analyses of drilling fluid and barium.

interface can rarely be done with a precision better than ±1 mm. Thus, even though the amount of cuttings in the samples were the same the concentration per gram sediment (wet or dry) may differ as result of the variable dilution with non-contaminated sediment. If the amount of drilling fluids and barium could be measured per sediment area, the scatter resulting from inaccurate sectioning would be eliminated.

Furthermore, in order to make mass balance considerations, the total amount of barium and drilling fluids per sediment area is required. This quantity is frequently estimated from concentrations per sediment weight and assumed mass-volume ratios of the dry or wet sediment. The mass per volume of the sediment may, however, vary considerably according to particle size and composition.

In the present experiment, the mass volume ratio was, in principle, determined in each sample by weighing sample containers before and after the sampling of the five core sections. The volume of the sample could be calculated from core diameter and sampling depth. In addition the water content of the pooled sample was determined by drying a subsample to constant weight at 90°C. Thus, the concentrations of barium and drilling fluids given in appendix table AI.2, were recalculated according to eq.2.1:

(eq.2.1) $$C_a = M_S \cdot (100-W) \cdot C_{wght} / 5 \cdot 100 \cdot A$$

in which

C_a = concentration per sediment area ($mg \cdot cm^{-2}$)
C_{wght} = concentration per dry sediment ($mg \cdot g^{-1}$)
M_S = total sample mass (g wet wght.)
W = water content (%)
A = sediment area sampled (cm^2)

Following this procedure errors resulting from inaccurate core sectioning and false assumptions of the mass-volume ratios were eliminated. The sediment area was taken to be the same as the core area. This was calculated from accurate measurements of the core diameter using a sliding calliper. If interactions between the core material and the samples produce a difference between sample area and core area an error may be introduced which will increase with decreasing core diameter. With the present core diameter of 16 mm, a 1 mm reduction of the sampled area would yield a 13% underestimation of C_a. Such errors would be of systematic nature, and no evidence have been found to support their presence. As shown in section 3.1.1, barium recoveries rather indicated the presence of a systematic error in the opposite direction.

2.4.3 Oxygen consumption

Oxygen consumption was determined two times a week by successive measurements of concentration of oxygen in the inlet water in the header tank (HT) and in the outlet water in the sampling cell (fig.2.1) on top of each chamber, using WTW oximeter and electrodes. The flow of water through each separate chamber was measured gravimetrically after collection of outflow water for at least 4 minutes.

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

(eq. 2.2) $$SOC = (C_i - C_o) \cdot F \cdot 10^3 / A \cdot 32$$

in which

SOC is the sediment oxygen consumption ($\mu mol \cdot m^{-2} \cdot h^{-1}$)
C_i is the concentration of oxygen in the water entering the chamber ($mg \cdot kg^{-1}$)
C_o is the concentration of oxygen in the water leaving the chamber ($mg \cdot kg^{-1}$)
F is the flow of water through the chamber ($kg \cdot h^{-1}$)
A is the area of the chamber (m^2)

The contribution to SOC from oxygen consumed by micro-organisms present in the water or attached to tubes and chamber walls was assumed to be small compared to the amount of oxygen consumed in the sediment. Furthermore, if the total background respiration is similar in control and treated chambers, the difference between treated and control sediment (ΔSOC) is a measure of the respiratory activity generated by the cuttings added.

2.4.4 Biogeochemical fluxes

Fluxes of carbon dioxide and inorganic micro-nutrient species NH_4^+, NO_3^- and PO_4^{3-} were determined once on day 161.

Two samples of chamber water were taken by inserting the tip of a 50 ml syringe through the outlet on top of each chamber. Three samples were similarly drawn from the header tank. The samples were preserved with a few drops of chloroform and stored at -20°C until analysed by standard methods for nutrient analyses at the NIVA laboratory. The flux was calculated using eq.2.1 after substitution of the concentration of oxygen with the mean concentration of the respective nutrients at the in- and out-let from each chamber.

The flux of CO_2 was determined from measurements of alkalinity and pH in the header tank and at the outlet from each chamber. The alkalinity was determined using the single acid addition method (Strickland and Parsons, 1968). An accurate volume of 50.0 ml of chamber water was pipetted into a bottle containing 15.0 ml 0.0100 M HCl. The alkalinity of the water was then calculated from the pH of the acidified sample. From *in situ* measurements of the pH in the header tank and the outlets from each chamber, the borate contribution as well as the concentrations of the various carbonic acid components could be calculated, using a spreadsheet program containing the appropriate equilibrium constants at the actual temperatures and salinities. The analytical procedure was very simple, but in order to obtain reliable estimates of the minute variations in pH and alkalinity, the utmost accuracy was required in pipetting and pH measurements.

2.4.5 Electrode measurements

Electrode measurements were done *in situ* by inserting electrodes directly into the submersed sediments at three different locations within each chamber. pH was measured using an Orion Ross 81-04 glass combination electrode. During the last two surveys, the pH was measured using a Sentron ion-specific field effect transistor (ISFET) pH-meter and sensor. Redox potentials were determined on a standard Radiometer P101 platinum electrode against the internal reference of the pH combination electrode. During the last two surveys the Eh was measured against an

Ag|AgCl reference electrode. The electrodes were inserted to successive positions 5, 15 and 25 mm below the sediment-water interface. The pH and redox potential were recorded as soon as the pH was stable.

Because of the high ionic strength of the seawater, the determination of the true pH of seawater is not straight forward. Also, long response times must be allowed before a stable reading can be taken when moving the electrode from a dilute pH-buffer to a seawater sample. In a previous study, a pH of 8.05 was found in the seawater taken supplied from 60m depth. At this depth, temporal variations of the pH of the fjord water are relatively small. Thus, throughout the experiment, pH was determined using the chamber water as a substandard with an assumed constant pH of 8.05. The pH of the chamber water was determined before and after the measurements in each chamber, and the pH values recorded in the sediment were corrected according to the deviation of the chamber water from the substandard value of 8.05. 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 redox potential 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) and the half-cell potential of the Ag|AgCl electrode should be 231 mV. The E_h of the samples were obtained by adding 431mV or 231 mV, respectively, to the potential recorded on the Pt-electrode. Thus, as recommended by ZoBell (1946), the electrode assemblies were checked, but not calibrated with the redox buffer.

2.4.6 Reproducibility of pH and E_h measurements

In a previous test, the reproducibility of the pH measurements in similarly treated sediments was found to be .09 pH-units. The corresponding reproducibility of the E_h was 33 mV. If these reproducibilities are taken to be valid also for the present test, 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.

3 RESULTS AND DISCUSSION

3.1 DRILLING FLUIDS AND BARIUM

3.1.1 Recovery of the cuttings added

On day zero, 300 g wet cuttings was added to each of the six chambers treated with drilling fluids. 500 g (wet wght.) of a non-contaminated sediment was added to each of the two control chambers. The water content was approximately 60% in the sediment and 12-15 % in the cuttings added. Thus, similar particle loads were added to all chambers.

The content of barium and drilling fluids in the cuttings added (table 3.1) was calculated from concentrations determined in subsamples of the cuttings taken during test set-up on day zero (given in Appendix III).

The concentrations of barium of 4.6-8.8 $mg \cdot cm^{-2}$ observed in the sediment on day two, tended to be slightly higher than the predicted concentrations of 4.8-5.9 $mg \cdot cm^{-2}$ (table 3.1). Because some loss of barium would be expected to occur during test set-up, the range of recoveries of barium of 96-155 % (mean = 122 %, std.dev. = 17 %, n=12), indicated the presence of some systematic error causing an underestimation of barium in the cuttings added or an overestimation in the sediment.

If the barite and drilling fluid components of the mud do not separate neither in the cuttings sample nor in the sediment, any error affecting the distribution of barium will have a similar effect on the distribution of drilling fluids. The concentrations of drilling fluids observed in the PAO- and AQM-chambers gave recoveries of 93-160 % (mean = 116 %, std.dev. = 26 %, n = 8), which indeed was very similar to the recoveries of barium. Thus, the source of this error should be sought in factors which may affect the distribution of cuttings particles. This implies that the error will more likely be found in set-up or sampling procedures or assumptions required for estimation of recovery, than in the chemical analyses of barium and drilling fluids.

In the PTF-chamber, recoveries of esters of 189-266 % and an increase of the DF:Ba ratio from 1.19 in the cuttings sample to 2.10 in the sediment sample, revealed a rather large error which must have affected the distribution of Petrofree esters independently of the barium present in the cuttings particles. One possibility is that fractionation had occurred in the cuttings sample, so that the subsample taken for GC-analyses have contained less ester, but similar amounts of barium, than the two subsamples added to the chambers. The higher concentration of olefins observed in chamber PAO 3 as compared to chamber PAO 6 (table 3.1) may have resulted from a similar problem with the Novadril cuttings sample.

The low concentration of esters in the cuttings samples indicated by the retort analyses resulted in high initial concentrations of drilling fluids in both Aquamul chambers.

Table 3.1. Initial treatment of experimental chambers and recovery of drilling fluids (DF) and barium (Ba) on the sediment surface on day 2.

Substance added	Chamber & sample	Added: $g \cdot ch^{-1}$ wet sed	Added: $mg \cdot cm^{-2}$ Ba	Added: $mg \cdot cm^{-2}$ DF	Added: ratio DF:Ba	Observed Day 2: $mg \cdot cm^{-2}$ Ba^5	Observed Day 2: $mg \cdot cm^{-2}$ DF	Observed Day 2: ratio DF:Ba	Recovered Ba	Recovered DF
Clean test sediment	CON 5	500	0.8	<.005	<<	0.0	<.005	<<	-	-
		"	"	"	"	"	"	"	-	-
Novadril Cuttings	PAO 3a	300	4.8	6.6	1.37	5.81	10.5	1.81	122 %	160 %
	PAO 3b	"	"	"	"	5.39	9.37	1.74	113 %	143 %
	PAO 6a	"	"	"	"	4.94	6.49	1.31	104 %	99 %
	PAO 6b	"	"	"	"	4.57	6.51	1.42	96 %	99 %
	Mean PAO 3&6					*5.18*	*8.22*	*1.57*	*109 %*	*125 %*
	Relative standard deviation					*±10 %*	*±25 %*	*±15 %*	-	-
Petrofree Cuttings	PTF 1a	300	5.9	7.0	1.19	7.57	17.7	2.34	129 %	255 %
	PTF 1b	"	"	"	"	7.69	16.6	2.16	131 %	238 %
	PTF 4a	"	"	"	"	8.41	18.5	2.20	143 %	
	PTF 4b	"	"	"	"	7.70	13.1	1.71	131 %	189 %
	Mean PTF 1&4					*7.84*	*16.5*	*2.10*	*134 %*	*237 %*
	Relative standard deviation					*±5 %*	*±14 %*	*±13%*	-	-
Aquamul Cuttings	AQM 2a	300	5.7	13.1	2.32	6.64	12.2	1.84	117 %	93 %
	AQM 2b	"	"	"	"	6.80	14.0	2.05	120 %	106 %
	AQM 7a	"	"	"	"	8.81	17.6	2.00	155 %	134 %
	AQM 7b	"	"	"	"	5.91	12.3	2.07	104 %	93 %
	Mean AQM 2&7					*7.04*	*14.0*	*1.99*	*124 %*	*107 %*
	Relative standard deviation					*±18 %*	*±18 %*	*±5 %*	-	-

Furthermore, fractionation in the cuttings sample may have resulted in the high initial concentrations in both Petrofree chambers and PAO 3. Thus, the objective of an initial concentration of about 5 $mg \cdot cm^{-2}$ was only approached in PAO 6.

The magnitude of the initial concentration may affect test results. In a previous experiment on degradation of mineral oil, respiration rates were found to level out at a concentration of THC of about 50 $mg \cdot cm^{-2}$ (Bakke et al, 1989). On the other hand, with regard to test standardisation, equal dose of cuttings (300 g) might be considered no less relevant than equal dose of drilling fluids.

Table 3.2. Concentrations of drilling fluids observed in each chamber during the test period. Units = $mg \cdot cm^{-2}$.

Day	PAO 3	PAO 6	AQM 2	AQM 7	PTF 1	PTF 4
2	9.37-10.5	6.49-6.50	12.2-14.0	12.3-17.6	16.6-17.7	13.1-18.5
62	7.55	4.91	14.3	17.8	11.98	9.34
111	5.67	4.46	13.3	12.3	10.58	6.19
161	5.74-6.20	3.48-4.07	5.75-9.90	10.3-11.2	5.85-7.67	2.35-2.97

[5] Excess barium, corrected for back-ground concentration of 0.8 $mg \cdot kg^{-1}$ dr. sed.

Table 3.3. Concentrations of barium observed in each chamber during the test period. Units = mg·cm^{-2}.

Day	PAO 3	PAO 6	AQM 2	AQM 7	PTF 1	PTF 4
2	6.57-6.12	5.40-5.77	7.61-7.79	6.89-9.75	8.38-8.50	8.65-9.30
62	6.87	5.21	8.03	10.15	8.29	8.58
111	6.04	4.87	9.97	8.21	8.25	8.61
161	6.01-6.79	3.61-4.80	4.86-7.67	7.50-7.98	7.35-7.51	7.72-8.51

Table 3.4. Mean drilling fluid:Ba ratios ± one standard deviation (σ_{n-1}) in cuttings sample and sediment during the test period.

	PAO	AQM	PTF
Control sed.	<0.01	<0.01	<0.01
Cuttings	1.37	1.22	1.19
Sediment			
Day 2	1.57 ± .24	1.21 ± .08	1.89 ± .26
Day 62	1.20 ± .08	1.17 ± .05	1.27 ± .25
Day 111	1.11 ± .02	0.72 ± .08	1.00 ± .40
Day 161	0.87 ± .08	0.72 ± .03	0.62 ± .35

3.1.2 Loss during the test period

Results of the chemical analyses of drilling fluids and barium are given in tables 3.2, 3.3 and appendix I. Time trends for each treatment are shown graphically in fig. 3.1. Curves and curve equations plotted in fig. 3.1 were calculated by exponential regression analyses assuming that eq. 3.1 were more representative than a linear function for the behaviour of drilling fluids after deposition on the sediment surface:

(eq.3.1) $C = C_0 \cdot 10^{-kt}$

in which:

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

From eq. 3.1 it can be shown that if the half-life τ is the time at which $C = C_0/2$, $\tau = \log 2/k$.

3.1.2.1 Drilling fluids

The regression curves plotted in fig.3.1 show the best fit of the data to a model of the general form given in eq.3.1. Because of different concentration levels in the two replicate chambers, some of the scatter in fig. 3.1 can be removed by normalising against concentrations observed in each chamber on day 2. Normalisation had no effect

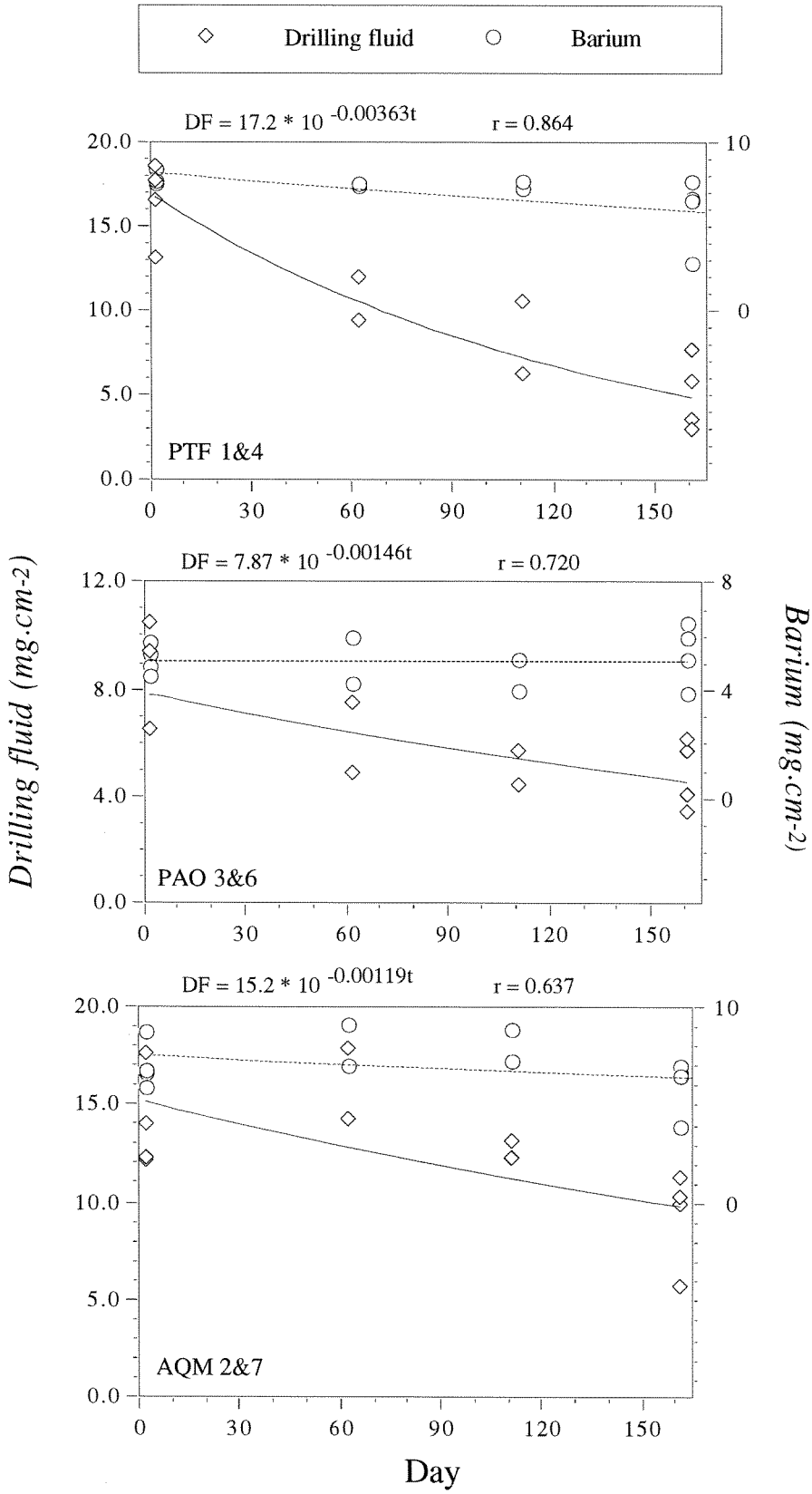

Fig. 3.1. Time trends of concentration of drilling fluids (diamonds, full line, left-hand ordinate) and barium (circles, dotted line, right-hand ordinate) in each chamber. Curve equations derived from exponential regression analyses are shown for drilling fluids only. Correlation coefficients, probabilities and confidence intervals for barium as well as drilling fluids are given in tables 3.4-3.8.

Table 3.5. Exponential regression analyses of time trends of normalised concentrations of Petrofree esters and ester:barium ratios in chambers 1 and 4 (see text). All p-values less than 0.05 and corresponding half-lives are highlighted.

PTF chamber no.:		PTF 1	PTF 4	PTF 1&4	PTF 1	PTF 4	PTF 1&4
Parameter:		DF	DF	DF	DF:Ba	DF:Ba	DF:Ba
Number of analyses	n	6	6	12	6	6	12
Correlation coefficient	r	0.965	0.976	0.882	0.968	0.982	0.869
Probability	p	**0.0018**	**0.0009**	**0.0001**	**0.0015**	**0.0005**	**0.0002**
Intercept ($mg \cdot cm^{-2}$)	C_0	1.0243	1.0678	1.05	1.0106	1.0745	1.04
Rate constant	k*1000	-2.49	-4.74	-3.63	-2.11	-4.46	-3.29
95 % Lower Confidence	k*1000	-3.42	-6.21	-4.99	-2.87	-5.64	-4.61
95 % Upper Confidence	k*1000	-1.56	-3.27	-2.27	-1.35	-3.28	-1.97
Half-life (days)	τ	**121**	**64**	**83**	**143**	**68**	**92**
95 % Lower Confidence	τ	**88**	**49**	**61**	**105**	**54**	**66**
95 % Upper Confidence	τ	**194**	**92**	**133**	**224**	**92**	**153**

Table 3.6. Exponential regression analyses of time trends of normalised concentrations of Novasol II olefins and olefin:barium ratios in chambers 3 and 6 (see text). All p-values less than 0.05 and corresponding half-lives are highlighted.

PAO chamber no.:		3	6	3&6	3	6	3&6
Parameter:		DF	DF	DF	DF:Ba	DF:Ba	DF:Ba
Number of analyses	n	6	6	12	6	6	12
Correlation coefficient	r	0.932	0.974	0.951	0.942	0.802	0.748
Probability	p	**0.0069**	**0.0010**	**0.0001**	**0.0050**	0.0548	**0.0052**
Intercept ($mg \cdot cm^{-2}$)	C_0	0.97	0.99	0.98	1.04	0.98	0.97
Rate constant	k*1000	-1.46	-1.45	-1.46	-1.39	-0.54	-0.96
95 % Lower Confidence	k*1000	-2.25	-1.92	-1.80	-2.08	-1.09	-1.56
95 % Upper Confidence	k*1000	-0.67	-0.98	-1.13	-0.70	0.02	-0.36
Half-life (days)	τ	**207**	**208**	**207**	**217**	559	**315**
95 % Lower Confidence	τ	**134**	**157**	**168**	**145**	277	**194**
95 % Upper Confidence	τ	**451**	**308**	**267**	**431**	-15100	**839**

Table 3.7. Exponential regression analyses of time trends of normalised concentrations of Aquamul ethers and ether:barium ratios in chambers 2 and 7 (see text). All p-values less than 0.05 and corresponding half-lives are highlighted.

Aquamul chamber no.:		2	7	2&7	2	7	2&7
Parameter:		DF	DF	DF	DF:Ba	DF:Ba	DF:Ba
Number of analyses	n	6	6	12	6	6	12
Correlation coefficient	r	0.686	0.681	0.669	0.871	0.976	0.908
Probability	p	0.1325	0.1361	**0.0173**	**0.0241**	**0.0009**	**0.0001**
Intercept ($mg \cdot cm^{-2}$)	C_0	1.11	1.0639	1.09	1.03	1.0151	1.02
Rate constant	k*1000	-1.42	-0.95	-1.19	-0.84	-0.72	-0.78
95 % Lower Confidence	k*1000	-3.50	-2.36	-2.11	-1.49	-0.95	-1.03
95 % Upper Confidence	k*1000	0.67	0.47	-0.26	-0.18	-0.50	-0.52
Half-life (days)	τ	213	318	**254**	**360**	**419**	**387**
95 % Lower Confidence	τ	86	128	**143**	**203**	**318**	**293**
95 % Upper Confidence	τ	-451	-643	**1162**	**1678**	**604**	**581**

Table 3.8. Exponential regression analyses of time trends of normalised concentrations of barium observed in the six benthic chambers treated with cuttings (see text). All p-values less than 0.05 and corresponding half-lives are highlighted.

Chamber		PTF 1	PTF 4	PAO 3	PAO 6	AQM 2	AQM 7	All
Parameter	Symbol	Ba	Ba	Ba	Ba	Ba	Ba	Ba
Number of analyses	n	6	6	6	6	6	6	36
Correlation coefficient	r	0.931	0.710	0.178	0.831	0.361	0.222	0.406
Probability	p	**0.0070**	0.1143	0.7353	**0.0403**	0.4818	0.6719	**0.0141**
Intercept ($mg \cdot cm^{-2}$)	C_0	1.01	1.00	1.01	1.01	1.08	1.05	1.0261
Rate constant	k*1000	-0.36	-0.27	-0.07	-0.91	-0.58	-0.23	-0.41
95 % Lower Confidence	k*1000	-0.56	-0.65	-0.64	-1.76	-2.68	-1.62	-0.73
95 % Upper Confidence	k*1000	-0.16	0.10	0.50	-0.67	1.51	1.16	-0.09
Half-life (days)	τ	**839**	1119	4314	**332**		1313	**737**
95 % Lower Confidence	τ	**539**	465	472	**172**	113	186	**414**
95 % Upper Confidence	τ	**1888**	-3020	-604	**451**	-200	-260	**3356**

on rate constants (k) and half-lives (τ), but the confidence intervals were narrowed. The results of regression analyses on normalised concentrations are shown in tables 3.5-3.8. The calculations were performed using StatView®II statistical software.

In the Petrofree and Novadril chambers (Table 3.5-3.6), p-values of ≤ 0.05 showed significant loss of drilling fluids in all chambers. The two Novadril chambers gave almost identical half-lives of 207-208 days. Thus, the 50% higher initial concentration in PAO 3 appeared to have no impact on the rate of loss of this drilling fluid. By pooling the data from both chambers, a half-life of 207 days and a confidence interval of 168-267 days was found for the Novasol II olefins.

For the Petrofree ester the half-life of 121 days in PTF 1 was large compared to the 64 days found in PTF 4. The difference could not be ascribed to different initial concentrations (Table 3.2). Regression analyses of the pooled data gave a half-life of the Petrofree esters of 83 days and confidence interval from 61 to 133 days. In several previous (and later) studies, the half-life of Petrofree esters at initial concentration levels at about 5 $mg \cdot cm^{-2}$ have been found to be close to 20 days. Thus, the present results indicated that seabed remediation will be slowed down at high initial loads of this drilling fluid.

In the Aquamul chambers (table 3.7) the concentration data were more scattered. Only regression analyses of data pooled from both chambers gave a statistically significant loss of Aquamul ethers. The half-life was 254 days, and the confidence interval of 143-1162 days showed the large uncertainty of the rate of loss of Aquamul ethers.

3.1.2.2 Barium

Barium may be considered a conservative property of the cuttings. Thus, after deposition, concentrations of barium should only change as a result of loss of cuttings particles by sampling, resuspension or burial to sediment layers below the sampling depth of two cm.

As shown in table 3.8, negative slopes indicated a small loss of barium from all treatments. Statistically significant loss ($p < 0.05$) was only observed in PTF 1 and PAO 6. The data gave no evidence that the different treatments had any impact on the rate of loss of barium. As shown in the right-hand column of table 3.8, pooling of all barium observations gave significant loss with a p-value of 0.014. The half-life of 737 days corresponded to a loss during the experimental period of 12% of the initial concentration of barium. The rather large confidence interval of 414-3356 days should be considered a result of the relatively short experimental period of less than 1/4 of the half-life.

3.1.2.3 DF:Ba ratio

Any loss of barium resulting from loss of cuttings particles via processes such as sampling, resuspension or burial, should be associated with a corresponding loss of drilling fluids. Furthermore, non-representative sampling of the cuttings particles, may cause random errors in the concentrations of drilling fluids and barium, but not in the concentration ratios. Thus, the change of the drilling fluid:barium ratio might be a better measure on biodegradation than the change of the concentration of drilling fluids alone. The problem is of course, that other random errors which are specific to each of the two concentrations, may add up to increase the scatter of the ratios.

Several analyses of non-polluted control sediments gave concentrations of 0.8 $gBa \cdot kg^{-1}$ dry sediment. This background concentration was subtracted from the total concentration of barium before calculation of the ratios shown in table 3.4 and fig 3.2.

In the two Petrofree chambers, half-lives calculated from the DF:Ba ratios were consistent with the half-lives calculated from the concentration of drilling fluids (table 3.5). Because of the small loss of particulate barium, the half-life of the ester:barium ratio was approximately 10% larger than the half-life of the ester.

In the PAO-chambers (table 3.6) the decrease of the olefin:barium ratio in chamber 6 was not significant at 95% ($p=0.055$). This was primarily a result of the anomalous rapid loss of barium observed in this chamber (table 3.3 and 3.7). Therefore, the ratios observed in PAO 6 were rejected and considering, again, the small loss of particulate barium, the half-life of 217 days for the Novasol II:Ba ratio in chamber 3 was consistent with the half-life of 207 days calculated from the Novasol II concentration data.

In the AQM-chambers (table 3.7), much of the scatter was removed when normalising the concentration data against barium. This was best shown by the increase of the correlation coefficient from 0.669-0.686 for the concentration of ethers to 0.871-0.976 for the ether:barium ratio. Thus, the DF:Ba ratios gave the better estimates of the half-life of the Aquamul ethers. From the data pooled for both chambers the ratios gave a half-life of 387 days with a confidence interval of 293-581 days.

As shown in the summary of half-life calculations given in table 3.9, the lower confidence limit of 143 days for the half-life of Aquamul ethers was actually found to be less than the lower limits of 145-168 days for the Novasol II olefin and Olefin:Ba ratio. Thus, from the analyses of Aquamul ethers alone, it could not be concluded that the loss of Aquamul ethers were significantly more slow than the loss of Novasol II olefins.

The reduction of scatter of the Aquamul data when normalised against barium concentrations indicated the presence of a sampling problem with regard to Aquamul cuttings. In a previous test of Aquamul ethers (Schaanning, 1994), a spurious increase

of concentration of ethers was found in the chamber sediments during the first 30-60 days of the test. The increase was concluded to result from a loss of a non-consolidated fraction of ethers during sampling shortly after addition of cuttings. The fact that this initial loss appeared to be confirmed in the present test by the concentrations of barium (table 3.3), was a strong evidence that the "undersampling" of drilling fluids resulted from an "undersampling" of cuttings particles. If so, the half-life calculated from the ratios should be independent of the initial sampling error.

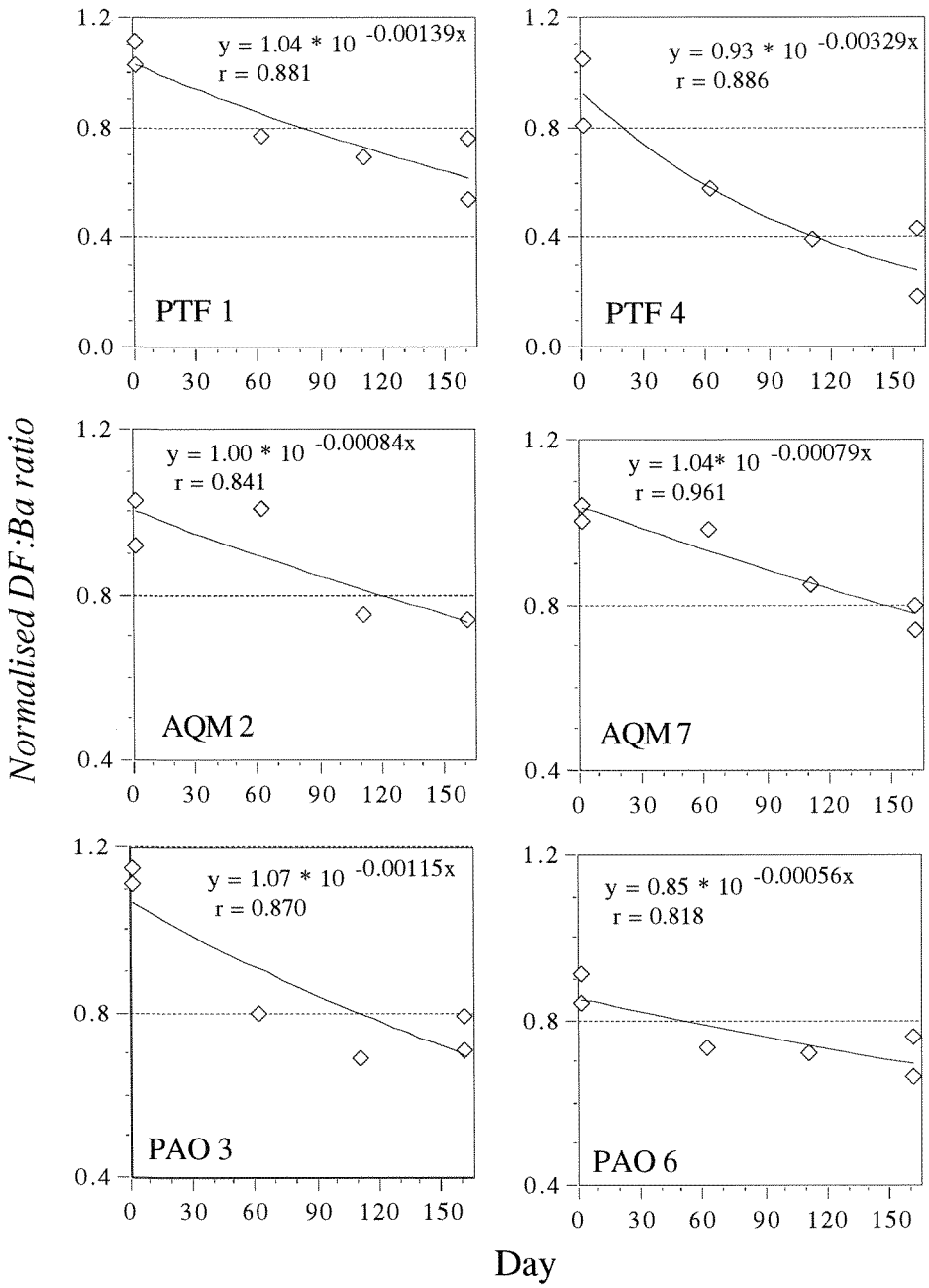

Fig. 3.2. Degradation of drilling fluids shown as the decline of drilling fluid:barium concentration ratios normalised against the mean ratio observed on day 2. Best fit exponential regression curves and correlation coefficients are shown for each chamber.

Table 3.9. Summary of results of half-lives calculated by regression analyses of drilling fluids and DF:Ba ratios.

Treatment	Half-life	Confidence interval	r	Chambers
Aquamul ether:Ba	387	293-581	0.908	2&7
Aquamul ether	254	143-1162	0.669	2&7
Novasol II olefin:Ba	217	145-431	0.942	3
Novasol II olefin	207	168-267	0.951	3&6
Petrofree ester:Ba	92	66-153	0.869	1&4
Petrofree ester	83	61-133	0.882	1&4

As shown in table 3.9 and the right-hand column of table 3.7, the regression analyses on the ether:barium ratios pooled from the two chambers gave a highly significant correlation (r=0.908, p=0.0001). The fact that the half-life calculated from this analyses was as high as 387 days, resulted to a large extent from the simultaneous decrease of the concentrations of barium and ether during the last sampling interval (tables 3.2 and 3.3). Thus, no evidence was found that the long half-life of the ether:Ba ratio could in any way be associated with the initial sampling problem.

It appears reasonable to assume that biodegradation is the predominant process altering DF:Ba ratios. Thus, as shown in table 3.9, even though the rate of total loss of Aquamul ethers (half-life = 254 days, confidence interval = 143-1162 days) was not clearly different from the loss of Novasol II olefins (half-life = 207 days, confidence interval = 168-267 days), loss by biodegradation appeared to be slow (half-life = 387 days, confidence interval = 293-581 days) as compared to Novasol II olefins (half-life = 217 days, confidence interval = 145-431 days) and Petrofree esters (half-life = 92 days, confidence interval = 66-153 days).

Thus, the large difference between the half-lives calculated from the concentration of ether and the half-lives calculated from ether:barium concentration ratios, seemed to indicate that non-degradative processes played a more significant role in the removal of Aquamul ethers as compared to Novasol II olefins and Petrofree esters. In the following section, data from a previous test shall be utilised for further elucidation of the degradation of Aquamul ethers. Unfortunately, barium was not analysed during the previous test.

3.1.3 Loss of Aquamul ethers - previous and present test

Fig. 3.3 shows all observations of Aquamul ethers obtained in the present and previous test (Schaanning, 1994). The figure revealed several clearly underestimated concentrations in samples collected 2-3 days after addition of cuttings. Therefore, the concentrations were normalised against the mean concentration for each chamber during the period 32-64 days after addition of cuttings.

Results of the regression analyses are given in table 3.10. In the first column, the p-value of 0.0004 for all data (n=32), showed that the concentration decreased significantly over the experimental period, but the r-value of 0.586 revealed that a rather small fraction of the total variance was explained by this model.

Omitting the data obtained on day 2-3, the r-value increased from 0.586 to 0.799, but the intercept of 1.28 was very high as compared to any observed concentrations of Aquamul ethers. Furthermore, the recoveries calculated in table 3.1 showed that the observed initial concentrations were more than large enough to account for the ethers added. Therefore, a more realistic initial concentration and a similarly good regression coefficient (r=0.809) was obtained by assuming that the exponential decrease was preceded by a lag phase of 64 days, during which no degradation of Aquamul ethers occurred. As shown in the right-hand column in table 3.10, this assumption gave a half-life of the Aquamul ethers of 138 days and a confidence interval of 103-208 days.

Thus, compared to the ether half-life of 143-1162 days calculated from the present test results (table 3.9), consideration of data from both tests, rejection of all observations on day 2-3 and the assumption of a lag phase of 64 days, resulted primarily in a more narrow confidence interval.

In order to compare the environmental impact of the assumption of a lag phase preceding exponential decrease, the loss of drilling fluids from the sediments during the first two years after a bulk sedimentation of cuttings, was calculated from the half-lives and confidence intervals given in table 3.9 and the right-hand column of table 3.10. The results are shown in table 3.11.

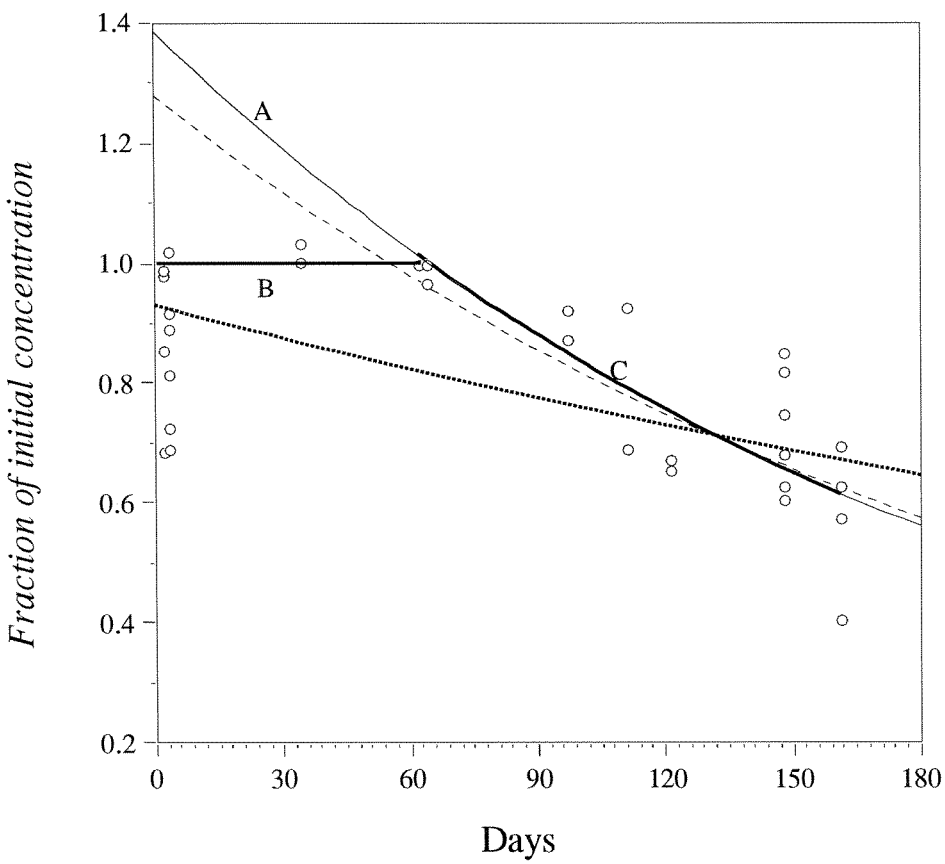

Fig. 3.3. All concentrations of Aquamul B+BII observed in the four chambers studied during present and previous tests. The concentrations were normalised against mean concentration measured in each chamber 32-64 days after addition of cuttings. The three plotted lines (dotted, broken and full) are regression curves. Result of the regression analyses are given in table 3.10. Dotted line = all data. Broken line = omitted day 2-3. Full line = omitted day 2-32. Best fit was found to be represented by a lag phase (curve B) followed by exponential decrease (curve C).

Table 3.10. Exponential regression analyses of time trends of normalised concentrations of Aquamul B + BII ethers. Data from four chambers operated during two different tests. All 32 observations and the three regression curves are plotted in fig. 3.3 (see text).

Parameter		all data no lag phase dotted line	omit day 2-3 no lag phase broken line	omit day 2-3 64 days lag phase full line (A+C)
Number of analyses	n	32	22	22
Correlation coefficient	r	0.586	0.799	0.809
Probability	p	0.0004	.0001	0.0001
Intercept	C_0	0.99	1.28	-
Half-life (days)	t	343	156	138
95 % Lower Confidence	t	227	116	103
95 % Upper Confidence	t	719	240	208

Table 3.11. Loss of drilling fluids from sediments in one and two years, respectively, after bulk sedimentation. Estimated loss was calculated from the lag phase and the half-life given in the two left-hand columns. Lower and higher loss was calculated using the 95% upper and lower, respectively, confidence limits of the half-life, as given in tables 3.9 and 3.10.

	Days Lag	Halflife τ	*% lost in one year* Est.	Lower	Higher	*% lost in two years* Est.	Lower	Higher
Total loss								
Petrofree ester, this test	0	83	95	85	98	99.8	98	99.98
Novasol II olefin, "	0	207	71	61	78	91	85	95
Aquamul ether, "	0	254	63	20	83	86	35	97
" , both test	64	138	78	63	87	97	89	99
Loss by biodegradation								
Petrofree:Ba, this test	0	92	94	81	98	99.6	96	99.95
Novasol:Ba, "	0	217	69	45	83	90	69	97
Aquamul:Ba, "	0	387	48	35	58	73	58	82

Assuming, then, that biodegradation was the primary process responsible for the change of DF:Ba ratios, biodegradation could account for 94% of the total loss of 95% of the Petrofree esters during the first year. Similarly, biodegradation could account for 69% of the total loss of 71% of the Novasol II olefins, but no more than 48% of the total loss of 63-78% of Aquamul B+BII ethers.

The latter result might indicate that particle removal is a more important process controlling the loss of Aquamul ethers. However, the observed loss of barium during the present test gave no evidence for any difference between the rates of particle loss from the three treatments. Thus, the larger difference between the loss of Aquamul ethers, as calculated from concentration data and ratios, respectively, may have been the result of larger sampling errors which resulted in poor fits of the concentration data to the exponential model and the subsequent assumption of a lag phase. The slow change and good model fits of the ether:Ba ratios, did however, indicate that biodegradation of Aquamul ethers was considerably slower than the biodegradation of the Novasol II olefins.

3.2 OXYGEN CONSUMPTION

Results of the sediment oxygen consumption measurements are given in tables 3.10 and 3.11 and in figs. 3.3-3.6.

3.2.1 Apparent fluctuations and curve smoothing

In plots of dense series of data, the clarity of trends may be blurred by frequent spikes and oscillations. Curve smoothing is a mathematical technique to reduce the amplitude of spikes by taking into account nearby data. Thus, a very simple smoothing technique is to replace each observation with the mean value of the actual and its preceding and succeeding observations. In this report, a 3-point binomial function integrated in the CricketGraph™ graphic software, was applied on the results of the sediment oxygen consumption.

As shown in table 3.12, the smoothing function had no effect on the mean rates of

Table. 3.12 Effects of the 3-point binomial function on the range, mean and cumulative sediment oxygen consumption in each chamber during the 161 days experimental period. Based on a total number of 51 analyses in each chamber. Units: concentrations in $\mu molO_2 \cdot m^{-2} \cdot h^{-1}$, cumulative SOC in $mmolO_2 \cdot m^{-2}$, differences are given as smoothed in % of non-smoothed.

	CON-3	CON-8	PAO-3	PAO-6	AQM-2	AQM-7	PTF-4	PTF-1
Smoothed								
Minimum	55	75	237	254	164	310	391	388
Maximum	290	372	747	882	678	730	2473	2058
Mean	151	184	453	494	454	509	1454	1186
Cumulative	583	713	1770	1935	1771	1988	5864	4749
Non-smoothed								
Minimum	-18	29	196	207	42	257	318	345
Maximum	327	649	786	984	792	811	2661	2240
Mean	151	184	453	494	454	509	1454	1186
Cumulative	581	713	1766	1935	1773	1980	5868	4736
Difference (%)								
Range	68	48	86	81	69	76	89	88
Mean	100.0	100.0	100.0	100.0	100.0	100.0	100.0	100.0
	100.3	100.0	100.2	100.0	99.9	100.4	99.9	100.3

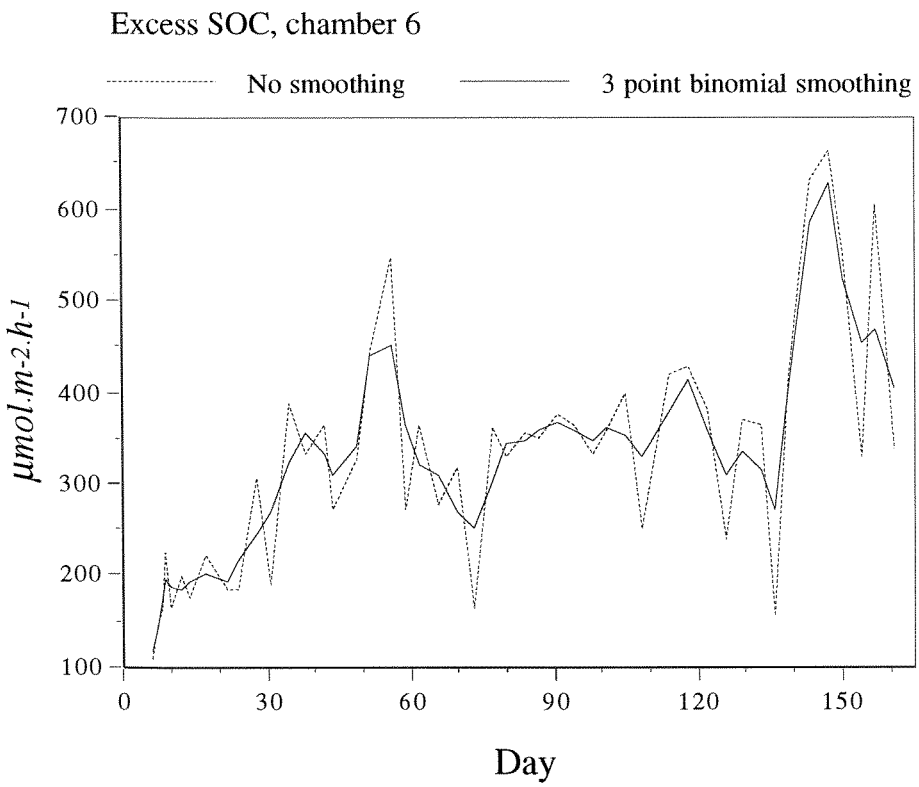

Fig. 3.4. Comparison of smoothed and non-smoothed excess rates of oxygen consumption in chamber PAO-6. Smoothing was performed using a three-point-binomial function integrated in the CricketGraph™ graphic software.

oxygen consumption. The effects on the cumulative consumption or weighted mean rates, were less than 0.4%. The range of the 51 analyses of SOC performed in each chamber, was however, reduced to 48-89% of the range of the non-smoothed data.

A graphic example on the effect of smoothing is shown in fig.3.4. The non-smoothed curve showed frequent spikes of considerable amplitudes. All chambers showed similar and simultaneously occurring spikes, and it appeared rather unlikely, that these spikes resulted from real variations in respiration rates in the chambers.

The residence time of the chamber water was approximately 20-30 hours. Ideally, then, the determination of the concentration drop resulting from oxygen consumed within the chamber only, requires that the concentration in the inlet water is constant over a period of time of more than 24 hours. Oxygen electrodes revealed that fluctuations up to 0.5 mg $O_2 \cdot l^{-1}$ might occur from one day to the next. Thus a recent rise of oxygen concentrations in the inlet water would yield an overestimated flux and *vice versa*. Nevertheless, at the present frequency of oxygen flux determinations, such errors will be averaged out in the time-series.

The magnitude of such errors will depend on the magnitude and timing of the oxygen variations in the header tank during the period preceding the observations. However, eq.2.1 showed that the absolute magnitude of the error will be proportional to the flow of water through the chamber. In order to maintain similar oxygen levels in all chambers, the chambers having a high consumption of oxygen were run with a higher flow. Thus, the amplitude of the apparent fluctuations will be larger in chambers having the higher rates of SOC. The flow was adjusted several times during the experiment.

The mean flow for the experimental period was 18-23 ml·min^{-1} in control chambers and 33-38 ml·min^{-1} in AQM, PAO and PTF-1, and 50 ml·min^{-1} in PTF-4. This seemed to explain much of the difference between the amplitudes of the fluctuations as they appeared in fig.3.5.

However, the major kick-backs observed in the PTF chambers during the 90-120 and >140 days periods, were too large to be explained by oxygen variations in the inlet water. This, indicated that variations in the quality of the inlet water, at least during these two periods, may have triggered some real variation in sediment metabolism which superimpose on the apparent fluctuations.

As shown in fig.3.4, curve smoothing was an efficient way to improve the clarity of the time-trends. The smoothing will have little effect on broad spikes like the ones observed

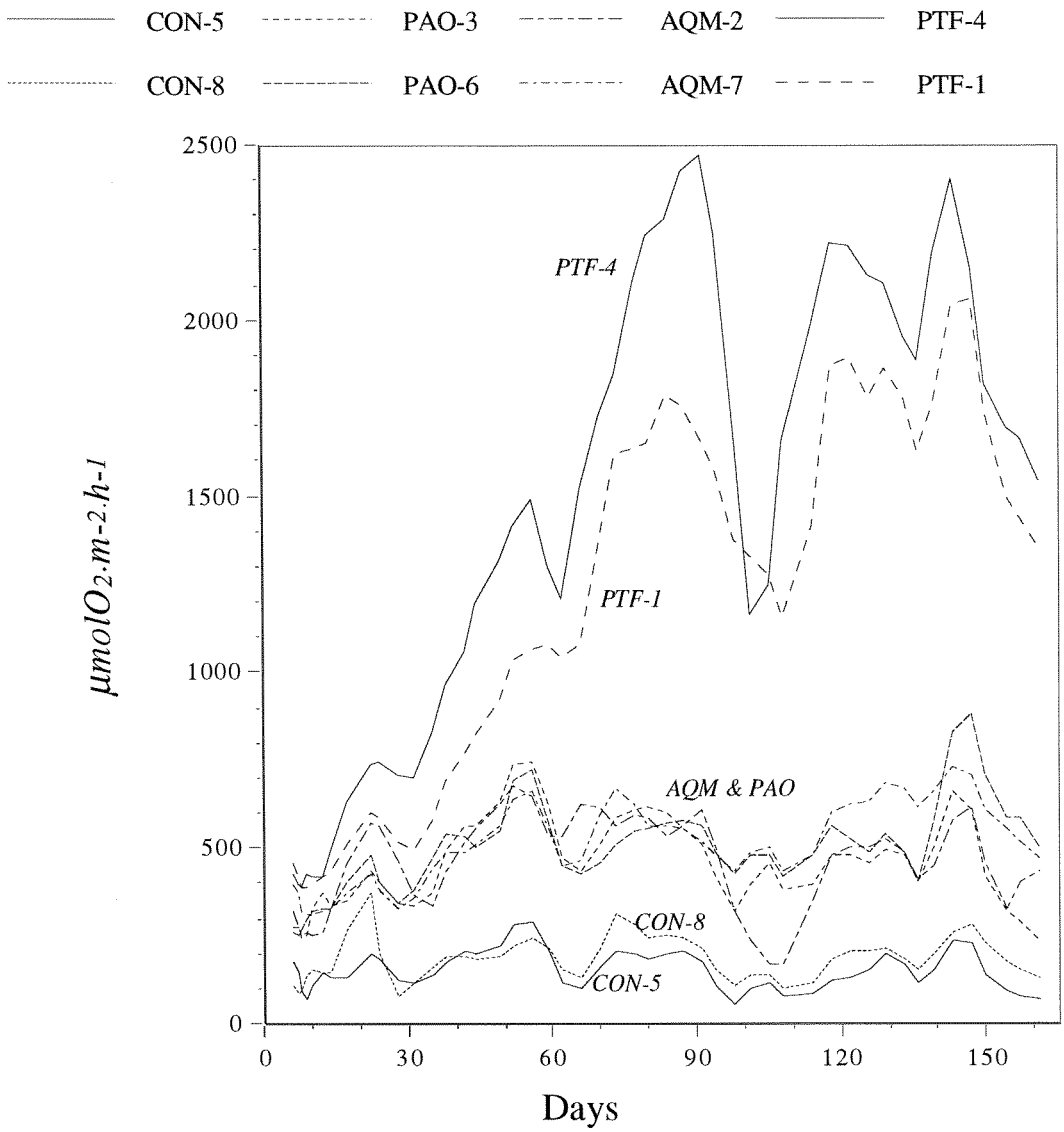

Fig. 3.5. Sediment oxygen consumption rates in each chamber. Data were smoothed using a 3 point binomial function.

during the 90-120 and >140 days periods. Thus, if the narrow spikes really were artefacts of oxygen concentration fluctuations in the inlet water, the smoothed curve should in fact be the one closer to the true rates of oxygen consumption.

3.2.2 Cumulative SOC

Fig.3.5 showed no obvious difference between instantaneous rates of SOC in the PAO and AQM chambers. The four curves occurred in a bundle with numerous cross-overs throughout the experimental period. Neither did the plot of the cumulative oxygen consumption in fig.3.6, reveal any differential behaviour of the two treatments.

As shown in table 3.12, the total oxygen consumption for the entire experimental period was 1770-1935 mmol$O_2 \cdot m^{-2}$ for the two olefin treatments and 1771-1988 mmol $O_2 \cdot m^{-2}$ for the ether treatments. Thus the differences between the replicate chambers were larger than the difference between the ether and olefin treatments.

In the control and ester chambers, respectively, 583-713 mmol $O_2 \cdot m^{-2}$ and 4749-5864 mmol $O_2 \cdot m^{-2}$ had been consumed during the experimental period. Thus, as compared to non-contaminated control sediments, approximate threefold increases of the sediment oxygen consumption were observed in the olefin and ether treatments and an eight-fold increase in the ester treatments. The higher oxygen consumption observed in PTF-4 as compared to PTF-1 (fig. 3.5), was consistent with the larger loss of esters observed in the sediments in chamber PTF-4 (fig.3.2 and table 3.2).

3.2.3 Time-trends

During the first determinations of SOC performed 6-10 days after addition of the cuttings, SOC was about 120 $\mu mol \cdot m^{-2} \cdot h^{-1}$ in control chambers as compared to 250-300 $\mu mol \cdot m^{-2} \cdot h^{-1}$ in the PAO and AQM chambers and 400 $\mu mol \cdot m^{-2} \cdot h^{-1}$ in the PTF chambers. During the following weeks a general increase of SOC was observed in all chambers. Thus, by day 55 characteristic rates were about 200 $\mu mol \cdot m^{-2} \cdot h^{-1}$ in the control, 650-750 $\mu mol \cdot m^{-2} \cdot h^{-1}$ in the PAO and AQM chambers and 1000-1500 $\mu mol \cdot m^{-2} \cdot h^{-1}$ in the PTF chambers. The SOC-rates observed in chamber PTF-4 were about 1.5 times higher than in PTF-1.

As shown in fig. 2.5, variations of the temperature and salinity of the inlet water were small throughout the initial 60 days period. Thus, the general increase of SOC rates might be the result of an adaptation period, during which the appropriate decomposer organisms colonised the recently prepared sediment surfaces.

After day 60, the water quality was more variable. Salinities were in general slightly lower, and the temperatures were up to 3°C higher (fig.2.5). As shown in table 3.11, the mean temperature in the header tank increased from 6.73°C during the first 59 days to 7.32°C for the 62-161 days period. From fig. 3.5 a temporary increase of SOC could be seen to occur in all chambers between days 62 and 76. This occurred simultaneous to a rise of temperatures from 6.5°C to 7.5°C. However, during the entire period after day 60, the mean rates of oxygen consumption in the control chambers were 166±33% as compared to 170±38% before day 60 (table 3.13). Thus, the increase of the mean

Table 3.13. Mean temperatures in header tank and mean SOC rates for each treatment during the 6-59 days period as compared to the 62-161 days period.

	6-59 days			62-161 days		
	Mean	±	% st.dev.	Mean	±	% st.dev.
Temperature (°C)						
HT	6.73	±	2	7.32	±	10
SOC rates ($\mu mol \cdot m^{-2} \cdot h^{-1}$)						
CON	170	±	38	166	±	33
PAO	432	±	35	503	±	22
AQM	431	±	30	518	±	21
PTF	715	±	43	1752	±	18

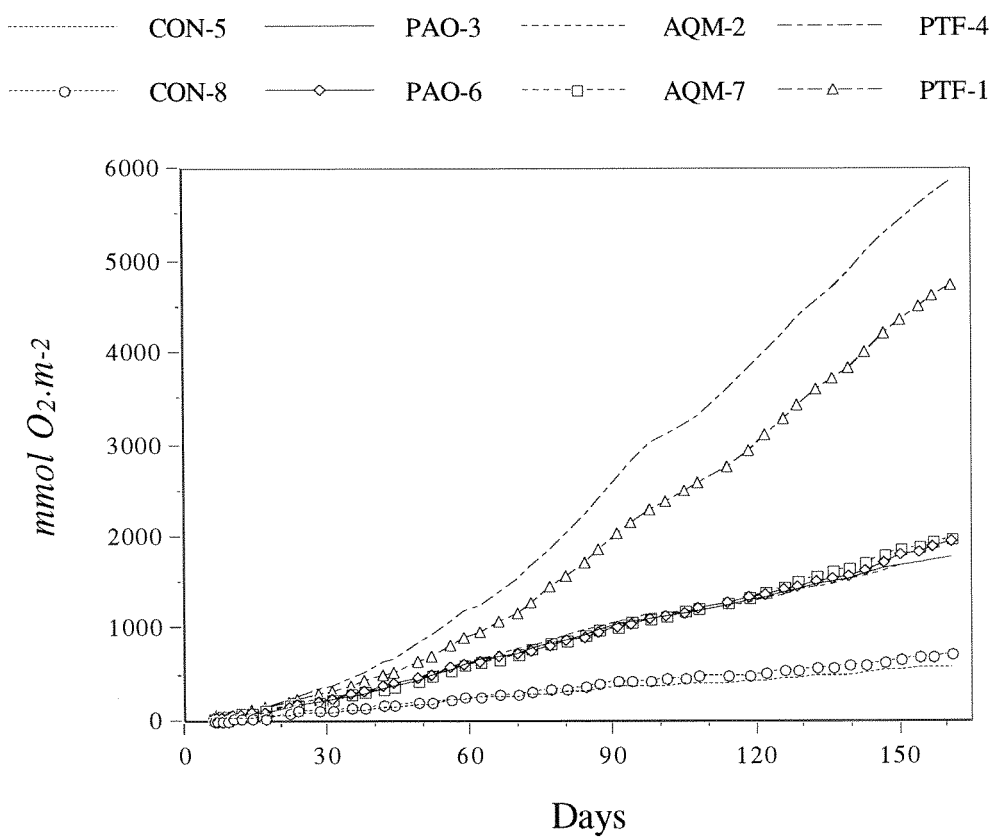

Fig.3.6. Cumulative sediment oxygen consumption in each chamber during the 161 days experimental period.

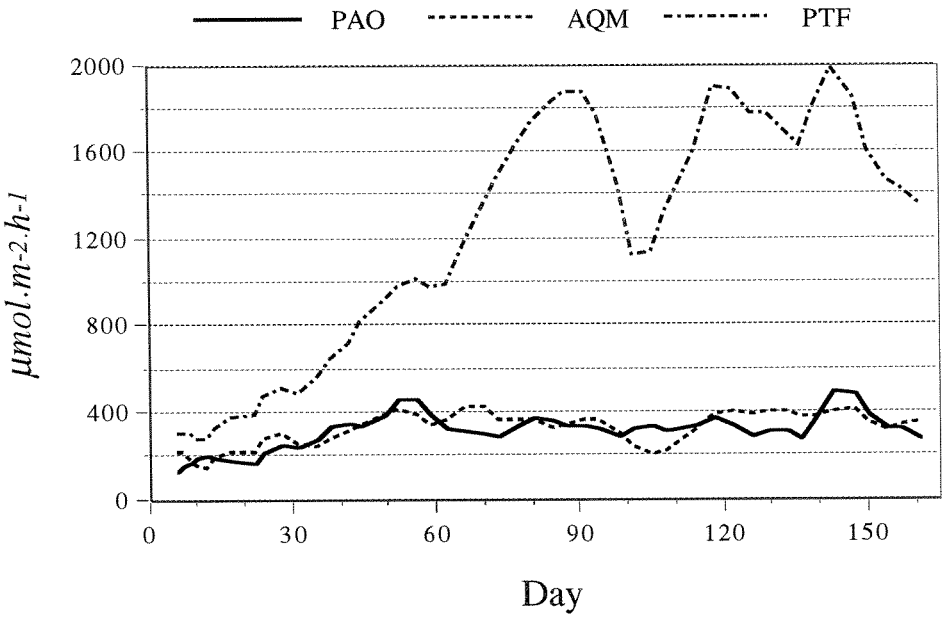

Fig.3.7. Time trend of mean excess oxygen consumption in sediments treated with Novadril PAO, Aquamul ethers and Petrofree esters.

temperature of 0.6°C had no significant impact on the oxygen consumption rates in the control chambers.

However, as shown in table 3.13, all chambers treated with cuttings had higher rates of oxygen consumption during the latter period and the variability, given as the relative standard variation, was less. The absence of a corresponding increase in the control chambers, showed that the increase in any of the chambers was not likely to result from the change of the water temperature.

If then, the increasing rate of SOC observed during the initial 59 days period was the result of adapting decomposer communities, the rates should remain high for as long as labile organic matter was present in the sediment. The fact that drilling fluids were abundant in all treated chambers by the end of the experiment (chapter 3.1), showed that this was indeed the case in all chambers treated with cuttings.

In the control chambers, however, any source of labile organic matter should be small and rapidly burned out. Short periods of elevated SOC-rates in the control chambers might result from degradation events triggered by the occasional sedimentation of organic material introduced from the fjord water. If so, similar inputs should occur in all chambers yielding no net effect on the excess rates. However, the moderate variations observed in the control chambers were rather spurious, and the data give no evidence for anything but more or less random fluctuations, which frequently may have been mere artefacts of the oxygen variations in the header tank.

As shown in chapter 3.2.1, the most extreme spikes in the SOC profiles, were reduced by curve smoothing. By subtraction of the SOC in the control chamber from the simultaneously observed SOC in the treated chambers, much of the scatter resulting from apparent as well as real variations of back-ground respiration, was further reduced. Thus, the excess rates of SOC shown in fig. 3.7 should represent the best available estimates of the respiration of drill fluid decomposer organisms.

As shown in fig. 3.7, the major kick-back of SOC-rates observed in the PTF chambers between day 90 and 120 could not be removed neither by curve smoothing nor subtraction of control respiration. The kick-back might result from microbial succession in the highly anoxic sediments of the PTF chambers. However, simultaneous minima were observed in several chambers (fig.3.5) and the period was characterised by relative strong temperature fluctuations (see fig.2.5). Being too large and lasting too long to be explained as an artefact of oxygen variations in the inlet water, the events of the oxygen consumption rates in the PTF-chambers during the 90-120 days period were most likely real variations in the respiration rates, triggered by variations in the water quality.

The fact that there was still a considerable pool of esters left in the sediment by the end of the experimental period as well as the fact that decreasing SOC rates were observed in all chambers, indicated that the decrease of SOC in the PTF chambers towards the end of the period, was the beginning of a second major kick-back rather than the beginning of the termination of the decomposition event.

Thus, the variations of the excess SOC plotted in fig.3.7, indicated that the first 60 days of the experiment represented an initial phase, during which decomposer communities were adapting themselves to the environmental conditions and the respective drilling fluid substrates. During the second phase, which lasted throughout the remaining 100 days of the experiment, high and relatively stable rates of oxygen consumption were observed in the treated chambers. This phase was probably controlled by stable decomposer communities metabolising the drilling fluids at the maximum rates allowed by substrate degradability or environmental factors. The much higher rates of SOC in the ester chambers showed that, given an easy degradable source of organic matter, the seabed environment has a potential for biodegradation at much faster rates than those observed for the ether and olefin treatments.

3.3 BIOGEOCHEMICAL FLUXES ON DAY 161

3.3.1 Ammonium, nitrate and phosphate

The degradation processes occurring in the sediments will not only be a major factor controlling the pore water environment and fluxes of oxygen, but also the fluxes of metabolic endproducts and biological key species such as CO_2, ammonium (NH_4^+), nitrate (NO_3^-) and phosphate (PO_4^{3-}). The determination of the fluxes of these species might yield further information on the predominant biological processes occurring in the sediment.

Ammonium is abundant in the protein fractions of organic matter. High concentrations of ammonium in pore waters and corresponding fluxes to the water mass has been frequently observed to result from recent sedimentation of natural organic matter. Orthophosphate is a key compound in the electron transport chains in living cells. Like with ammonium, high concentrations frequently indicate biodegradation in a stagnant environment, whereas a depleted environment indicates biosynthesis and lack of nutrients. Relative to carbon, the contents of phosphate and ammonium in the base fluids should be much smaller than the average marine biological ratios of 106 atoms of carbon and 16 atoms of nitrogen for each atom of orthophosphate (the so-called Redfield ratios). For this reason fertilisers have been added to increase biodegradation of mineral oil spills (Leahy and Colwell, 1990).

Table. 3.14. Nutrient fluxes ($\mu mol \cdot m^{-2} \cdot h^{-1}$) determined on day 161. Negative flux means uptake in chamber, positive flux means release. Below each flux the 95% significance of the difference between the nutrient outflow from each treatment is compared to the corresponding nutrient inflow and to the outflow from the control chambers, respectively. (See text).

	NH_4^+	NO_3^-	PO_4^{3-}
CON mean flux	1.3	-2.1	0.3
Sign. diff. outlet vs inlet	no	no	no
PAO mean flux	4.8	-18	0.7
Sign. diff. PAO vs CON	yes	yes	yes
Sign. diff. outlet vs inlet	no	no	no
AQM mean flux	3.6	-23	-0.4
Sign. diff. AQM vs CON	yes	yes	no
Sign. diff. outlet vs inlet	no	yes	no
PTF mean flux	6.9	-62	-2.2
Sign. diff. PTF vs CON	yes		yes
Sign. diff. outlet vs inlet	no	yes	yes

Nutrient fluxes determined on day 161 are given in table 3.14. Concentrations of nutrients were determined in two samples of the water flowing out from each chamber and three samples of the water in the header tank. The fluxes were then calculated as shown in eq.2.1 after substitution of SOC with the respective nutrient. The crucial step in this procedure was to obtain a significant difference between the flow of nutrients into and out of each chamber without lowering the flow rate to a level at which oxygen concentrations would drop down below 50% saturation. Therefore, the significance of this difference was estimated by comparison of the four molflows (= concentration · flow) from each treatment to the three molflows entering from the header tank, using the ANOVA analyses of variance in the StatView®II statistical software. A similar procedure was used for comparing the outflow from each treatment with the outflow from the control chambers. The results of both analyses are given in table 3.14.

Table 3.14 showed release of ammonium and uptake of nitrate in all chambers. Ammonium ions are energetically more favourable than nitrate ions as a source of amino-nitrogen for protein synthesis. Thus, even though not significant at the 95% level, the consistent release of ammonium from all treatments did not indicate any shortage of nitrogen nutrients in the pore water. In spite of the fact that adsorbed PO_4^{3-} is known to be mobilised during the reduction and dissolution of ferric oxides in anoxic sediments, a significant uptake of phosphate was observed in the ester chambers. This uptake was, however, consistent with the depletion of phosphate in the pore waters of sediments treated with mineral oil cuttings reported in Bakke et al (1989). Possibly, the PO_4^{3-}-nutrient requirement of the bacteria associated with the degradation of esters, was larger than the supply from mineralogenic and other sources in the sediment. When the concentration of PO_4^{3-} in the pore water decrease to values less than the concentration in the chamber water, the diffusive flux will be directed into the sediment, as observed in the PTF chambers.

Alternatively, adsorption of PO_4^{3-} on reprecipitated iron oxides might account for the net uptake in the PTF-chambers. Reprecipitated ferric oxides appeared to be abundant in the outlet tubes downstream the sampling site, but no reddish precipitates could be seen inside the chambers at this stage of the decomposition event.

The uptake of nitrate was, significant in the AQM and PTF treatments. The three times higher uptake in the PTF-chambers as compared to AQM and PAO was similar to the relative magnitudes of the SOC-rates (fig. 3.5), indicating a coupling between the metabolic systems controlling the two fluxes. In the sediments, bacteria reduce nitrate to various species such as NO_2, N_2O, N_2 and NH_4^+. The reduction of 1.00 mole of nitrate to molecular nitrogen is equivalent to the consumption of 1.25 mole oxygen. Thus, if the entire nitrate uptake of 60 $\mu mol \cdot m^{-2} \cdot h^{-1}$ (table 3.14) was used for decomposition of drilling fluids via denitrification, the amount of drilling fluids mineralised via denitrification on day 161 could account for no more than 5% of the mineralisation via oxygen respiration, which occurred at a rate of 1400 $\mu mol \cdot m^{-2} \cdot h^{-1}$ (fig.3.5).

3.3.2 Carbon dioxide

Because of the contribution from anaerobe degradation processes which may release CO_2 without the consumption of a corresponding amount of oxygen, the flux of CO_2 is a better measure of carbon mineralisation than the flux of oxygen. Like with the nutrient fluxes, the crucial step in the procedure is to obtain a significant decrease in concentration between the header tank and the outflow from each chamber. The procedure is somewhat more laborious than the oxygen determinations and requires the utmost precision in sampling techniques and pH measurements.

Results of CO_2 flux measurements are shown in table 3.15. Mean fluxes were 165 $\mu mol \cdot m^{-2} \cdot h^{-1}$ in the control chambers, 300 $\mu mol \cdot m^{-2} \cdot h^{-1}$ in AQM, 550 $\mu mol \cdot m^{-2} \cdot h^{-1}$ in PAO and 800 $\mu mol \cdot m^{-2} \cdot h^{-1}$ in PTF. Because of the considerable variation between similarly treated chambers the difference between the fluxes of ΣCO_2 in AQM and PAO was not significant. Thus, as was observed for the oxygen consumption in the olefin and ether treatments throughout the experimental period, the difference between the replicate chambers of the flux of ΣCO_2 on day 161, were larger than the difference between the treatments.

However, the range of $O_2:\Sigma CO_2$ flux ratios of 0.4-0.8 in the control and PAO chambers, were nearly invariable and clearly lower than the ratios of 1.1-3.8 observed in the AQM- and PTF-chambers. Thus, the $O_2:\Sigma CO_2$ flux ratios in the PAO resembled those of the control chambers and were clearly lower than those of the ether and ester treatments. The fact that the fluxes were similar, whereas the ratios differed, indicated a qualitative difference between the degradation communities in the PAO and AQM chambers. If the electrons transferred to sulphate are passed on to oxygen rather than being stored in the sediments in reduced species such as S(-II), S(0), Fe(II) and Mn(II), the $O_2:\Sigma CO_2$ flux ratio should be 1.0 in chambers dominated by aerobe respiration and sulphate reduction. During the initial phase of an event of sulphate reduction, reduced species may accumulate in the sediment, and ratios <1.0 might be expected to occur. When sulphate reduction rates decrease towards the end of a decomposition event, oxidation of some of the reduced species produced during the initial stages may yield ratios >1.0.

As shown by the proliferation of black sulphide-bearing sediments and lowering of the redox potentials, the abundance of reduced species had increased during the early stages of degradation in the ester chambers. Obviously, oxygen consumed by the delayed reoxidation of H_2S and other reduced species, could well have been responsible for the ratios >1.0 observed in the PTF-chambers. The larger cumulative SOC and the greater

Table 3.15. Fluxes of oxygen and ΣCO_2 and O_2:ΣCO_2 flux ratios determined in each chamber on day 161.

Chamber	Uptake O_2 $\mu mol \cdot m^{-2} \cdot h^{-1}$	Release ΣCO_2 $\mu mol \cdot m^{-2} \cdot h^{-1}$	O_2:ΣCO_2 Flux ratio
CON-5	70	160	0.4
CON-8	130	170	0.8
PAO-3	240	330	0.7
PAO-6	500	770	0.6
AQM-2	430	230	1.9
AQM-7	470	370	1.3
PTF-1	1350	1200	1.1
PTF-4	1540	400	3.8

loss of drilling fluids observed in PTF-4 as compared to PTF-1 showed that the decomposition event had proceeded further in PTF-4. If so, the larger O_2:ΣCO_2 flux ratio should occur in PTF-4, as observed (table 3.15).

Neither redox potentials nor colour changes revealed any significant sulphide accumulation in the AQM-chambers. A moderate but frequent lowering of the redox potentials were, however, observed in this treatment during the 28-111 days period (table 3.19 and fig.3.9). No corresponding lowering of the E_h was observed in the PAO chambers. A lowering of the redox potentials of the magnitudes shown in table 3.19, might probably occur as a result of increased abundance of highly electroactive Fe^{2+} and Mn^{2+}-ions.

If the lowering of the redox potentials was a result of increased abundance of reduced iron and manganese ions in the pore water, sulphate reduction is the only process likely to have produced the reducing agents required. As long as ferric and manganese oxides are present in the sediment, sulphide ions may be consumed in the reduction of mineral phases at similar rates as it was produced by sulphate reduction. Thus sulphate reduction may occur at considerable rates without any detectable accumulation of H_2S in the pore water.

As shown in table 3.4 the DF:Ba-ratios in the AQM-chambers decreased from 1.21 on day 2 to 0.72 on day 111. No decrease was, however, observed after day 111. This was different from the DF:Ba ratios of the olefin and ester treatments, which showed a more steady decrease throughout the experimental period. If a moderate rate of sulphate reduction had contributed to the ether degradation prior to day 111, a pool of reduced iron and manganese ions should might have been present in the sediment to lower redox potentials during this period. However, if the ether degradation ceased at about day 111, as was indicated by the stabilisation of the DF:Ba ratio, sulphate reduction should decrease and oxygen may have been consumed in reoxidation and precipitation of Fe(III)- and Mn(IV)-oxides.

PO_4^{3-} is known to adsorb strongly onto freshly precipitated iron oxides. Thus, an occurrence of reprecipitation of ferric oxides in the AQM-chambers towards the end of the experiment would not only explain the elevated $O2:\Sigma CO_2$ flux ratios, but might also explain an uptake of PO_4^{3-} in the AQM chambers. Even though not significant at the 95% level, a small net uptake was indeed observed on day 161 in the AQM-treatment, whereas a small net release of PO_4^{3-} was observed in the PAO-treatment.

As shown in this chapter, some rather interesting additional information and reasoning was derived from the results of the flux measurements on day 161. It should be kept in mind, however, that fluxes determined at one occasion only may not be very representative for fluxes integrated over a longer time interval. Thus, the observations of CO_2 and nutrient fluxes performed in this experiment were too few to be used for more than supporting evidence on the processes occurring in the various chambers. $O_2:\Sigma CO_2$ ratios other than 1.0 were assumed to be temporary occurrences, which should be counterbalanced by opposite deviations during other periods of the decomposition event. Thus, in order to estimate any possible error inherent in carbon mineralisation calculated from oxygen consumption rates, CO_2 fluxes must be determined at representative time intervals throughout the period considered.

3.4 MASS BALANCE OF DRILLING FLUIDS

3.4.1 Calculations and precautions

In this mass balance a distinction was made between:

- *Total loss* which was calculated from the difference between the initial and final concentration of drilling fluids,
- *particle loss* or *barium correction* which was calculated from the loss of barium and which either represent a real loss of drilling fluids by sampling, resuspension or burial of cuttings particles or an apparent loss resulting from sampling errors.
- *Mineralisation* was calculated from the oxygen consumption in each chamber and will represent ultimate bio-oxidation of the drilling fluids to CO_2 and water, whereas
- *biodegradation* will include mineralisation as well as any production of metabolites which emigrate from the sampled layer or escape the chemical analyses of the drilling fluid.
- *Other loss* is the mass balance deficit calculated from the difference between initial and final concentration plus specified loss items such as mineralisation and barium loss.

Biodegradation was not calculated explicitly but when barium was measured, the sum of mineralisation and other loss should represent the best available estimates of the biodegradation.

Table 3.16 Mass balance of drilling fluids on cuttings during the 0-161 days experimental period.

	PAO 3	PAO 6	**Mean**	AQM2	AQM7	**Mean**	PTF 1	PTF 4	**Mean**
Units = mg DF/cm2									
Final concentration, day 161	5.97	3.78	**4.87**	7.83	10.75	**9.29**	6.76	2.66	**4.71**
+ mineralised (oxygen eq.)	1.02	1.17	**1.10**	1.17	1.40	**1.29**	4.24	5.36	**4.80**
+ particle loss (Ba correction)	-0.09	1.60	**0.91**	3.13	4.24	**3.69**	2.05	1.51	**1.77**
+ other loss	3.03	-0.06	**1.33**	2.13	1.46		4.10	6.27	**5.20**
= initial concentration	9.94	6.50	**8.22**	14.26	17.85	**16.05**	17.15	15.80	**16.48**
Normalised									
Remaining fraction, day 161	0.60	0.58	**0.59**	0.55	0.60	**0.58**	0.39	0.17	**0.29**
+ mineralised (oxygen eq.)	0.10	0.18	**0.13**	0.08	0.08	**0.08**	0.25	0.34	**0.29**
+ particle loss (Ba correction)	-0.01	0.25	**0.11**	0.22	0.24	**0.23**	0.12	0.10	**0.11**
+ other loss	0.30	-0.01	**0.16**	0.15	0.08	**0.11**	0.24	0.40	**0.32**
= initial concentration	1.00	1.00	**1.00**	1.00	1.00	**1.00**	1.00	1.00	**1.00**

Table 3.17 Mass balance of ethers in chambers treated with Aquamul cuttings in present and previous test. Because of the sampling problem shortly after addition of cuttings, initial concentration of Aquamul ethers was calculated as mean of concentrations determined one and two months after addition (ref. chapter 3.1).

	This test		Previous test		**All tests**		
	AQM2	AQM7	AQM3	AQM8	**Mean**		**St.dev.**
Units = mgDF·cm^{-2}							
Final concentration	7.83	10.75	10.78	9.04	**9.60**	±	**1.43**
+ mineralised (oxygen eq.)	1.17	1.40	0.88	1.11	**1.14**	±	**0.21**
	5.26	5.70	0.97	3.12	**3.76**	±	**2.18**
= initial concentration	14.26	17.85	12.63	13.27	**14.50**	±	**2.33**
Normalised							
Final remaining fraction	0.55	0.60	0.85	0.68	**0.67**	±	**0.13**
+ mineralised (oxygen eq.)	0.08	0.08	0.07	0.08	**0.079**	±	**0.006**
+ other loss (particles incl.)	0.37	0.32	0.08	0.24	**0.25**	±	**0.13**
= initial concentration	1.00	1.00	1.00	1.00	**1.00**	±	**0.00**

Because of the spuriously low concentrations of barium and ethers in the Aquamul chambers on day 2, the concentrations determined on day 62 (table 3.2 and 3.3) was taken to represent the initial concentration of both Ba and ether.

Mineralisation was calculated from the accumulated excess oxygen consumption (table 3.10), and the theoretical amount of oxygen required to oxidise an average drilling fluid carbon atom to CO2. The conversion factors derived from the information available on the stoichiometric formula of each drilling fluid, were 3.43 mgO_2·mg olefin^{-1}, 3.01 mgO_2·mg ether^{-1} and 2.97 mg O_2·mg ester^{-1}.

Processes such as denitrification and fermentation, which might mineralise some organic carbon to CO_2 (or CH_4) without consuming a corresponding amount of oxygen, might contribute to the mass balance deficit. However, fermentation does not compete well with oxygen- and sulphate-respiration and was assumed to be negligible in the test chambers. As indicated by the consumption of nitrate on day 161 of 18-62 µmolNO_3

$m^{-2}h^{-1}$ (table 3.14), respiration by nitrate reduction (denitrification) could at most account for less than 5% of the oxygen respiration.

Respiration by sulphate reduction is, however, a quantitatively significant process in coastal sediments. The overall stoichiometry of sulphate reduction of a simple hydrocarbon unit can be assumed to follow:

Eq. 3.2 $$CH_2 + 6/8\ SO_4^{2-} + 12/8\ H^+ = CO_2 + 6/8\ H_2S + H_2O$$

The hydrogen sulphide produced is frequently assumed to be reoxidised to sulphate by chemical consumption of oxygen:

Eq. 3.3 $$6/8\ H_2S + 3/2\ O_2 = 6/8\ SO_4^{2-} + 12/8\ H^+$$

If such reoxidation was complete during the experimental period, the net result would be the sum of eq. 3.2 and 3.3:

Eq. 3.4 $$CH_2 + 3/2\ O_2 = CO_2 + H_2O$$

Thus, the mineralisation of drilling fluids by sulphate reducing bacteria would be measured as oxygen consumption. If, however, some fraction of the H_2S produced in Eq. 3.2 is oxidised by the reduction of electron acceptors other than O_2, the mineralisation of the drilling fluids would be correspondingly underestimated. Underestimation of the mineralisation of drilling fluids might also result from any presence of reduced sulphur such as H_2S or precipitated metal sulphides (FeS, FeS_2 and others), by the end of the experimental period.

Such underestimation of the mineralisation will show up as a corresponding increase of the "other loss". As shown by low redox potentials, the characteristic odour of H_2S, the presence of black sediments (FeS) and white spots on the sediment surface (elemental sulphur, S^0), as well as the very high ratio between oxygen consumption and release of carbon dioxide observed in PTF 4 on day 161 (table 3.15), which most probably resulted from chemical consumption of oxygen, various reduced compounds were present in the sediment towards the end of the experimental period. None of the other treatments showed any similar evidence for the presence of reduced species. In a more recent test performed with a low initial concentration of 3.1 $mg \cdot cm^{-2}$, 99% of the added ester was lost during the experimental period and as much as 80% of the loss could be accounted for by oxygen consumption. Therefore, most of the "other loss" observed in the Petrofree treatment (fig.3.5) may have been accounted for by mineralisation via sulphate reduction and the presence of a temporary large pool of reduced compounds.

Because of the hydrophobic nature of the base fluids, dissolution in the water flowing through the chamber is not very likely to represent a significant contribution to the "other loss" item. If dissolution was a significant process, a major loss should have been observed during test set-up when recently crushed and suspended cuttings were allowed to settle through the water-column. The recoveries shown in table 3.1, did not indicate any significant contribution from dissolution processes.

In the present mass balance (fig.3.5, tables 3.16 and 3.17) the sum of the mineralised fraction and "other loss" should represent a good approximation of the biodegraded fraction. Because barium was not determined in the previous test of Aquamul ethers, the loss of cuttings particles was included in the term "other loss" in the evaluation of Aquamul ethers in table 3.17 and fig. 3.5 (lower bar).

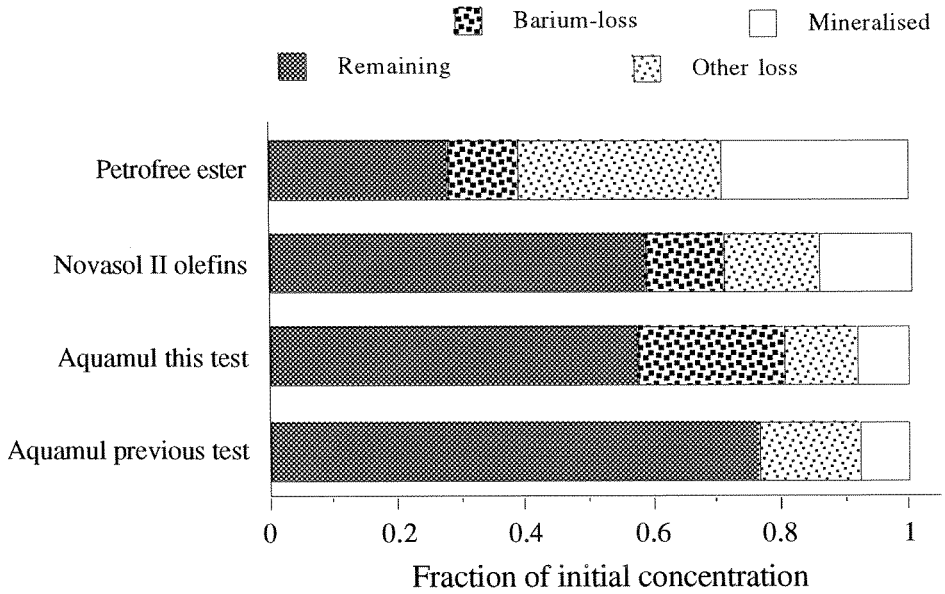

Fig. 3.5. Mass balance for each chamber in the present test and two chambers treated with Aquamul in previous test (AQM3 and AQM8).

3.4.2 Results of the mass balance calculations

As shown in fig. 3.5 and table 3.17, the mineralised fraction of the Aquamul ethers was 7-8% in all four chambers investigated during the present and preceding test. This was significantly less than the mineralisation of 10-18% of the Novadril II olefins and 25-34% of the Petrofree esters.

Also, biodegradation determined as the sum of the mineralised fraction and other loss was unquestionably larger in the Petrofree treatment as compared to the Novadril and Aquamul treatments. Because any loss of barium during the previous test might have been taken into the mass balance at the cost of the other loss fraction, fig. 3.5 seemed to suggest that not only the mineralisation, but also the total biodegradation of Novadril olefins was larger than the biodegradation of the Aquamul ethers. The comparison between the other loss of Novadril olefins and other loss of Aquamul ethers was, however obscured by the large variability of the barium loss between the two replicate Novadril chambers, the lack of barium data from the previous test and the inconsistency between the remaining fraction of Aquamul ethers in the two tests. The production of semi-degraded metabolites appeared to be the most likely process accounting for the other loss item in both treatments.

3.4.3 Biodegradation mechanisms

From a consideration of the molecular structure (appendix I) the Petrofree esters will most likely undergo a hydrolytic cleavage to yield C_{10}-C_{14} saturated fatty acids and 2-ethyl hexanol. Neither product will be determined in the ester analyses. The oxygen required for the enzymatic hydrolyses of the ester bond, should be small compared to the loss of ester. Indeed, during the first 60 days period, 49% of the total loss of esters occurred (table 3.1) at a consumption of only 18% of the total consumption of oxygen

(table 3.13, fig.3.7). Thus, the first 60 days may be considered an initial phase characterised by adaptation of the microbial community and cleavage of ester bonds.

If the cleavage reaction was fast compared to mineralisation or loss of the metabolites, the pool of alcohols and fatty acids should be expected to increase during the initial period. The fatty acids are easily available to rapid β-oxidation in the mitochondria of living cells and should be fit for supporting high rates of oxygen consumption. The sharp increase of the oxygen consumption rates observed in the Petrofree chambers shortly after day 60 (fig.3.17), and the maintenance of the high rates throughout the rest of the experimental period, indicated the evolution of a microbial community well adapted for exploitation of the ester metabolites. The simultaneous drop of the redox potential showed that sulphate reducers were an important component of this community.

As shown in fig. 3.17, initial periods of about 60 days of increasing rates of oxygen consumption, were also observed in both Aquamul and Novadril treatments. After the initial period, an oxygen consumption level of about 400 $\mu mol \cdot m^{-2} \cdot h^{-1}$ (in excess of the oxygen consumption rates observed in control chambers) was maintained throughout the remaining experimental period.

A very similar pattern of oxygen consumption was observed in the previous test of Aquamul ethers. In the report of that test (Schaanning, 1994), the degradation of the Aquamul ether was modelled as a two-step reaction: an initial hydrolytic cleavage of the ether bond followed by biodegradation of the metabolites. Hydrolytic cleavage of the Aquamul B and Aquamul BII ethers should yield mostly branched C_4, C_8 and C_{10} alcohols. Metabolisation of alcohols are thought to occur less easily than metabolisation of fatty acids and branching may further enhance biodegradation.

The GC-MS analyses revealed that Novasol II was a saturated $C_{20}H_{42}$ hydrocarbon. The broad peak area shown in the chromatograms in appendix I, indicated frequent branching of the Novasol molecules. Thus from the molecular structure, biodegradation of Novasol II might be expected to occur more slowly than the biodegradation of Aquamul ethers, in which the ether bond should represent a weak point available for an initial bacterial attack. Neither the mass balance consideration, nor the oxygen consumption rates gave any evidence for a more rapid degradation of the ethers. On the contrary, the mineralisation fraction was slightly higher (table 3.16 and 3.17) and the half-life tended to be somewhat shorter for the Novasol II olefins (table 3.9). These results may indicate steric hindrance of an enzymatic attack on the Aquamul ether bond.

On the other hand, ether:Ba ratios (table 3.4) revealed a major decrease during the 60-120 days period. The fact that this occurred without any significant elevation of the oxygen consumption rates, would be consistent with the low oxygen requirements of an enzymatic cleavage reaction as the predominant process responsible for the change of the ratio. If the rate of ether cleavage really peaked during the 60-120 days time interval, the initial lag phase assumed in fig. 3.3 might correspond to the time required for the evolution of an ether splitting enzyme system and the following exponential decrease would primarily represent the rate of the ether cleavage reaction.

Because of the uncertainties involved, primarily in the determination of concentrations of ethers, the importance of the ether cleavage reaction as a mechanism in seabed remediation may range from negligible to a major mechanism explaining the lag phase model for the degradation of the Aquamul ether. In any case, the cleavage of the Aquamul ether was very slow compared to the cleavage of the Petrofree ester.

3.5 EFFECTS OF ADDITION OF CUTTINGS

3.5.1 Visual effects

Visible changes on the sediment surface might be considered to be strong evidence of the occurrence of dramatic changes in the sediment environment.

When the turbidity had disappeared from the water column after the settlement of the cuttings and control sediments added, the sediment surfaces could be distinguished by slightly different colours. Thus, the AQM showed a characteristic red colour, whereas the other chambers contained various shades of grey. No individuals could be seen on the surface, but numerous holes and burrows revealed the presence of an active macrofauna community. Also numerous tracks on the sediment surface in chambers treated with cuttings, as well as in the control chambers, showed that animals had been quite actively moving about on the sediment surface. This might indicate a stress reaction promoted by the heavy sedimentation of particles.

Three dead individuals of brittle stars were observed on the sediment surface in AQM 2 and four in AQM 7. No dead individuals of any species were observed in any of the other chambers. This can hardly be interpreted as anything but some acute toxicity response to the ether cuttings.

On day 30, as throughout the remaining experiment, the AQM chambers maintained the characteristic red colour. The other chambers were mostly grey, but some small yellow and red patches had become visible on the surface in the two PTF chambers. Animal tracks were rather scarce, but numerous holes and mounds were present in all chambers.

During the remaining experimental period, no further changes were noted to occur in the AQM, PAO or control chambers. This could not be said of the PTF-chambers. On day 62, photographs taken of all sediment surfaces (APPENDIX IV) revealed the presence of large yellow-red and black spots in the PTF-chambers, and bacterial mats with white sulphur precipitates covered most of the sediment surface in both chambers. Several individuals of perished brittle stars were observed shrouded in the bacterial film on the sediment surface. The bacterial mats remained present throughout the rest of the experiment, and by day 111 the sediment surface had turned completely black with patches of white sulphur precipitates. A similar appearance was observed by the termination of the experiment.

3.5.2 Effects measured on pH and E_h electrodes

All measurements of pH and redox potentials are given in appendix table AI. Table 3.15 shows the observed mean values in control chambers. Large variations with time in control sediment should not occur. Thus, anomalous low potentials observed on days 3, 63 and 112, most probably resulted from systematic errors originating in malfunction of the measuring equipment. The difficulties were not completely overcome until the application of a different electrode assembly and electrode configuration during the final survey. Such systematic errors are outweighed in ΔE_h which is used throughout this study for assessment of effects.

The deviations from control sediments of the values recorded at 5 mm depth are shown in fig. 3.8 and the numeric deviations at all depths are shown in table 3.16. Table 3.16 also shows the statistical significance of the difference between treated and control sediments at the various depths and sampling days.

Table 3.15. Mean values and standard deviations (six determinations, two chambers) of pH and E_h observed in control sediments.

	pH						E_h (mV)					
Sed. depth:	5 mm		15 mm		25 mm		5 mm		15 mm		25 mm	
Day 3	7.74	± .05	7.65	± .07	7.71	± .06	92	± 32	17	± 36	-11	± 28
Day 28	7.75	± .09	7.57	± .11	7.44	± .05	184	± 40	99	± 11	68	± 13
Day 63	7.96	± .19	7.68	± .19	7.49	± .11	99	± 27	40	± 12	26	± 21
Day 112	7.79	± .06	7.62	± .09	7.37	± .10	102	± 32	59	± 16	30	± 11
Day 162	7.92	± .03	7.86	± .05	7.77	± .12	252	± 19	182	± 13	140	± 15

Table 3.16. pH and E_h deviations in treated versus control sediment. The right-hand columns show the result of statistical analyses of the variance (ANOVA) of the data. + or - means that the six observations of pH or E_h at the given depth in the two similarly treated chambers were significantly higher (+) or lower (-) than the corresponding observations in the two control chambers. n means that the difference was not significant. Significance level = 95%.

	Treated - control, numeric difference						Significant at 95%					
	ΔpH			ΔEh (mV)			ΔpH			ΔEh (mV)		
	5 mm	15mm	25mm	25mm	15mm	25mm	5	15	25	5	15	25
PAO-CON												
Day 2	.09	.03	-.06	18	28	-19	n	n	n	n	n	n
Day 28	-.18	-.14	-.06	-37	14	-7	-	n	n	-	n	n
Day 62	-.36	-.24	-.15	-10	24	18	-	-	-	n	+	n
Day 111	-.28	-.27	-.09	-16	0	1	-	-	-	n	n	n
Day 161	-.01	-.14	-.14	-65	-44	-55	n	-	-	-	-	n
AQM-CON												
Day 2	.47	.20	.07	31	21	23	+	+	n	+	n	n
Day 28	.08	.13	.11	-48	-31	-35	n	n	n	-	-	-
Day 62	-.39	-.27	-.19	-66	-23	-20	-	-	-	-	n	n
Day 111	-.17	-.21	-.09	-25	-7	-8	-	-	-	n	n	n
Day 161	-.03	-.10	-.09	-48	-26	-76	n	n	n	-	n	n
PTF-CON												
Day 2	.09	.04	-.02	42	36	-9	n	n	n	+	n	n
Day 28	-.40	-.30	-.12	-113	-51	-39	-	-	n	-	-	-
Day 62	-.54	-.27	-.09	-164	-107	-98	-	-	n	-	-	-
Day 111	-.29	-.13	.12	-338	-292	-271	-	-	-	-	-	-
Day 161	-.17	-.17	-.17	-344	-319	-291	-	-	-	-	-	-

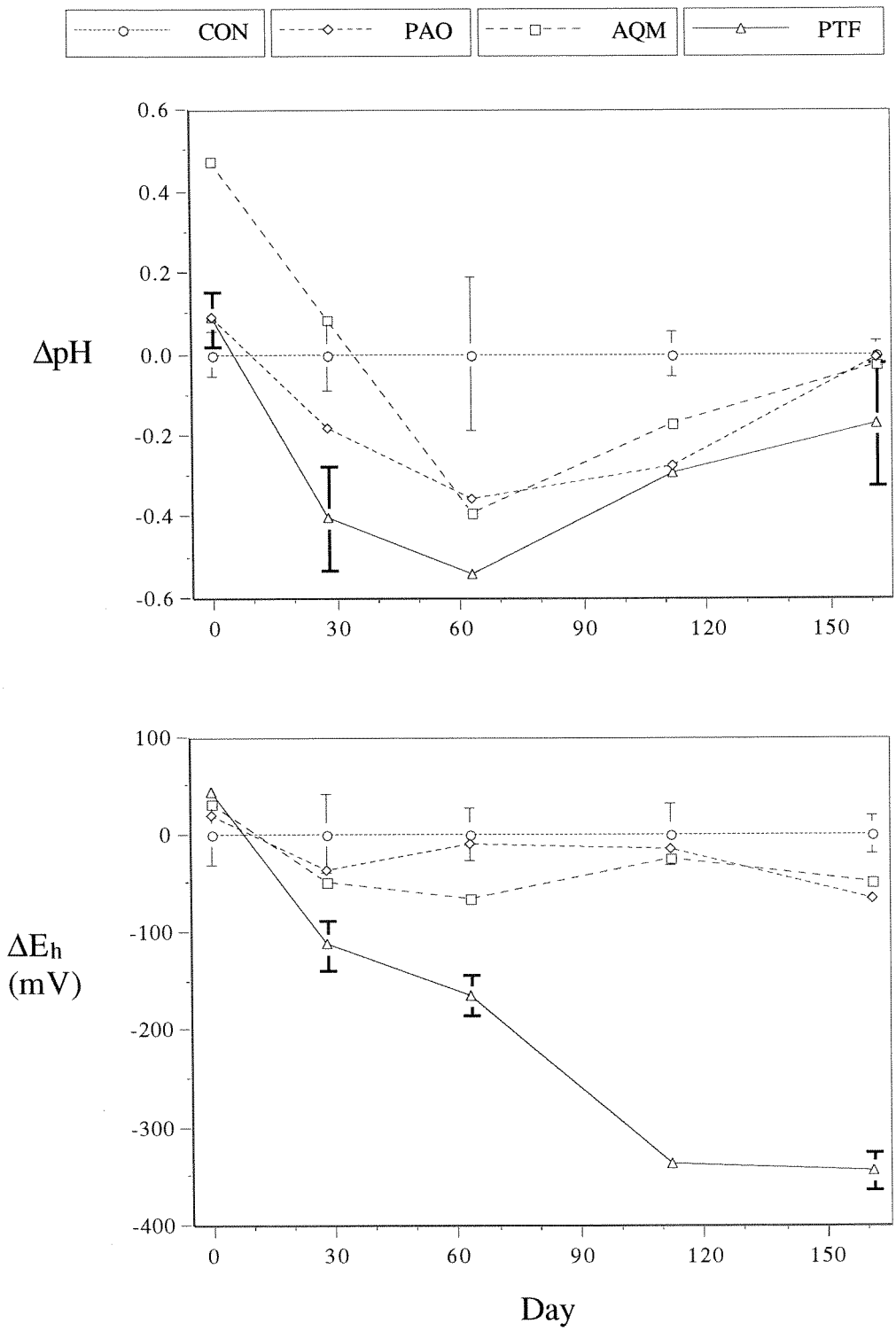

Fig.3.8. pH (upper plate) and E_h (lower plate) deviations from control sediment. Mean of six observations at 5 mm depth. Vertical bars equal two standard deviations on data from control and PTF chambers. For better clarity, standard deviations were not shown for the PAO and AQM treatments.

On day 2, a mean pH of 8.31 was observed at 5 mm depth in the AQM treatments. This value was significantly higher (table 3.16) than the pH of 7.84 observed in the control sediment and 7.93 in PAO- as well as the PTF-treated chambers. This initial pH-response has been observed in several previous tests, and results from lime or other carbonate or hydroxide salt buffers present in the mud system. The deviation declined with depth and was not significant at 25 mm depth.

On day 2, the lowest E_h values were observed in the control chambers. Thus, as shown in table 3.16, slightly positive deviations occurred throughout most of the treated sediments. Significant positive deviations were observed at 5mm depth in the AQM and PTF-chambers only.

After day 2, the pH decreased in all treated chambers. The maximum negative deviations of .36, .49 and .54 pH-units in the PAO-, AQM- and PTF-treatments, respectively, were all observed on day 61. During the period 61-161 days the pH of the treated chambers increased at 5 mm depth. Thus, by the end of the experiment, only the PTF treatments showed a significant negative deviation of pH. The magnitude of this deviation was 0.17 pH-units. Careful consideration of the results of the statistical analyses in table 3.16, revealed that the pH-decline appeared first at 5 mm depth, close to the cuttings layer, and penetrated slowly down into subsurface layers. Of the total number of 15 observations in each treatment, significant negative pH deviations were observed at 6 occasions in the AQM-treatment, 9 occasions in the PAO-treatments and 10 occasions in the PTF-treatments. Obviously, the alkaline buffer must account for the lower frequency of negative deviations in the AQM-chambers.

Also the E_h tended to decrease with time in the treated sediments. In the PAO-chambers a moderate decrease was observed at 5 mm depth at all surveys after day 2 and at all depths during the final survey. In the AQM treatments, negative deviations were slightly larger and occurred at all depths and surveys after day 2. The frequency of significant negative deviations was 3 of 15 in PAO- and 6 of 15 in the AQM-chambers. Thus, degradation of ethers appeared to yield slightly larger redox-effects than the degradation of olefins.

Much larger deviations of E_h were observed in the PTF chambers. Here the E_h decreased from a slight positive deviation on day 2 via negative deviations of 113 mV on day 28 and 164 mV on day 61 to a low level of 338-344 mV below the control sediments on days 111 and 161. The decrease was observed at all depths, but the maximum deviations occurred at 5 mm depth, close to the cuttings layer. As shown in table 3.16, the negative E_h deviation in the ester treatment were significant at all depths and surveys after day 2 yielding a frequency of 12 of 15 occasions. Thus, ester degradation caused the highest frequencies of significant negative deviations of both pH and redox potentials.

The large drop of E_h in the PTF chambers was a clear evidence of the abundance of hydrogen sulphide in these sediments. The more moderate deviations observed in the AQM-treatments might result from very low levels of sulphide activity, or more likely, an increased abundance of highly electroactive iron(II) and manganese(II) ions in the pore water.

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APPENDIX I: Tables of results.

Table AI.1. Recorded values of E_h and pH at 5 mm, 15 mm and 25 mm depth at the three locations in each chamber.

				pH			Eh (mV)		
	Trm.	Ch.no	S.no	5 mm	15 mm	25 mm	5 mm	15 mm	25 mm
Day 0	CON	5	1	7.83	7.77	7.78	151	73	25
Day 0	CON	5	2	7.84	7.83	7.89	94	25	-3
Day 0	CON	5	3	7.83	7.79	7.78	60	36	
Day 0	CON	8	1	7.78	7.73	7.84	96	-18	-17
Day 0	CON	8	2	7.94	7.64	7.72	78	-25	-50
Day 0	CON	8	3	7.81	7.73	7.83	71	8	-35
Day 0	PAO	3	1	7.96	7.81	7.79	143	12	-18
Day 0	PAO	3	2	7.97	7.72	7.61	123	75	-68
Day 0	PAO	3	3	7.77	7.64	7.68	92	5	-51
Day 0	PAO	6	1	7.97	7.82	7.75	149	119	-7
Day 0	PAO	6	2	7.98	7.84	7.81	97	45	-21
Day 0	PAO	6	3	7.93	7.83	7.81	56	10	-17
Day 0	AQM	2	1	8.30	7.85	7.79	152	50	5
Day 0	AQM	2	2	8.24	7.94	7.93	126	22	-34
Day 0	AQM	2	3	8.53	8.16	8.05	72	5	-4
Day 0	AQM	7	1	8.27	7.97	7.82	161	61	44
Day 0	AQM	7	2	8.36	7.87	7.81	115	48	35
Day 0	AQM	7	3	8.16	7.89	7.83	110	38	23
Day 0	PTF	4	1	7.85	7.79	7.84	132	5	-28
Day 0	PTF	4	2	7.91	7.77	7.72	129	83	-15
Day 0	PTF	4	3	7.89	7.79	7.80	118	12	-36
Day 0	PTF	1	1	8.04	7.87	7.77	146	104	6
Day 0	PTF	1	2	7.93	7.77	7.76	129	35	-38
Day 0	PTF	1	3	7.93	7.76	7.85	149	77	-12
Day 28	CON	5	1	7.85	7.66	7.57	166	86	85
Day 28	CON	5	2	7.81	7.54	7.47	162	103	62
Day 28	CON	5	3	7.89	7.60	7.50	169	110	72
Day 28	CON	8	1	8.03	7.85	7.62	265	110	74
Day 28	CON	8	2	7.78	7.64	7.55	172	97	64
Day 28	CON	8	3	7.89	7.70	7.54	167	87	48
Day 28	PAO	3	1	7.73	7.62	7.52	160	142	53
Day 28	PAO	3	2	7.85	7.48	7.38	135	108	74
Day 28	PAO	3	3	7.50	7.38	7.35	74	62	25
Day 28	PAO	6	1	7.66	7.55	7.55	178	119	89
Day 28	PAO	6	2	7.66	7.56	7.56	176	139	58
Day 28	PAO	6	3	7.78	7.55	7.53	155	106	62
Day 28	AQM	2	1	8.09	7.95	7.79	156	84	49
Day 28	AQM	2	2	7.94	7.78	7.66	129	67	30
Day 28	AQM	2	3	7.94	7.80	7.70	116	68	29
Day 28	AQM	7	1	8.11	8.02	7.79	148	94	42
Day 28	AQM	7	2	7.79	7.51	7.42	103	68	28
Day 28	AQM	7	3	7.88	7.71	7.54	159	25	19
Day 28	PTF	4	1	7.37	7.24	7.30	62	31	21
Day 28	PTF	4	2	7.61	7.42	7.38	55	55	45
Day 28	PTF	4	3	7.65	7.62	7.61	52	23	6
Day 28	PTF	1	1	7.45	7.31	7.46	115	88	59
Day 28	PTF	1	2	7.36	7.30	7.37	87	67	34
Day 28	PTF	1	3	7.39	7.32	7.41	55	25	5
Day 63	CON	5	1	8.21	8.05	7.70	143	53	29
Day 63	CON	5	2	7.76	7.49	7.42	67	18	-12
Day 63	CON	5	3	8.25	7.87	7.52	106	37	17
Day 63	CON	8	1	8.17	7.67	7.61	82	37	36
Day 63	CON	8	2	7.95	7.73	7.69	85	44	49
Day 63	CON	8	3	8.01	7.84	7.62	109	49	38

Day 63	PAO	3	1	7.74	7.53	7.47	97	59	36
Day 63	PAO	3	2	7.63	7.48	7.40	56	42	31
Day 63	PAO	3	3	7.87	7.62	7.48	62	40	26
Day 63	PAO	6	1	7.61	7.52	7.49	135	109	82
Day 63	PAO	6	2	7.64	7.50	7.35	95	75	53
Day 63	PAO	6	3	7.71	7.54	7.46	87	58	35
Day 63	AQM	2	1	7.79	7.60	7.49	28	5	-11
Day 63	AQM	2	2	7.70	7.59	7.42	36	30	16
Day 63	AQM	2	3	7.70	7.60	7.60	18	-17	-10
Day 63	AQM	7	1	7.69	7.45	7.32	31	23	7
Day 63	AQM	7	2	7.56	7.38	7.27	30	27	17
Day 63	AQM	7	3	7.57	7.42	7.31	52	35	21
Day 63	PTF	4	1	7.49	7.51	7.50	-55	-54	-63
Day 63	PTF	4	2	7.56	7.56	7.55	-82	-75	-84
Day 63	PTF	4	3	7.52	7.54	7.55	-67	-81	-69
Day 63	PTF	1	1	7.49	7.43	7.44	-85	-86	-98
Day 63	PTF	1	2	7.51	7.55	7.53	-72	-73	-77
Day 63	PTF	1	3	7.52	7.46	7.42	-28	-32	-39
Day 112	CON	5	1	7.87	7.63	7.34	144	84	49
Day 112	CON	5	2	7.91	7.71	7.41	128	68	34
Day 112	CON	5	3	7.95	7.83	7.60	53	38	21
Day 112	CON	8	1	7.96	7.82	7.57	95	58	29
Day 112	CON	8	2	7.84	7.69	7.42	87	52	23
Day 112	CON	8	3	7.83	7.63	7.45	105	56	21
Day 112	PAO	3	1	7.63	7.49	7.42	82	73	53
Day 112	PAO	3	2	7.58	7.43	7.37	106	77	24
Day 112	PAO	3	3	7.63	7.39	7.29	117	85	58
Day 112	PAO	6	1	7.54	7.42	7.35			
Day 112	PAO	6	2	7.68	7.47	7.40	67	35	14
Day 112	PAO	6	3	7.63	7.52	7.44	57	29	2
Day 112	AQM	2	1	7.75	7.61	7.48	63	27	-8
Day 112	AQM	2	2	7.80	7.57	7.41			
Day 112	AQM	2	3	7.69	7.51	7.33	64	45	-1
Day 112	AQM	7	1	7.63	7.42	7.26	102	75	50
Day 112	AQM	7	2	7.73	7.44	7.35	80	64	47
Day 112	AQM	7	3	7.73	7.49	7.40			
Day 112	PTF	4	1	7.59	7.58	7.58	-231	-241	-242
Day 112	PTF	4	2	7.61	7.59	7.58	-230	-232	-246
Day 112	PTF	4	3	7.58	7.55	7.55	-231	-240	-256
Day 112	PTF	1	1	7.61	7.61	7.60	-232	-227	-236
Day 112	PTF	1		7.59	7.59	7.59	-243	-232	-237
Day 112	PTF	1	3	7.62	7.60	7.60	-246	-222	-230
Day 161	CON	5	1	8.02	8.03	8.02	228	161	139
Day 161	CON	5	2	8.05	7.98	7.91	246	195	151
Day 161	CON	5	3	8.07	7.98	7.96	234	187	158
Day 161	CON	8	1	8.00	7.92	7.80	272	177	149
Day 161	CON	8	2	8.00	7.92	7.71	260	194	125
Day 161	CON	8	3	7.99	7.90	7.80	270	179	119
Day 161	PAO	3	1	8.05	7.81		147	105	-95
Day 161	PAO	3	2	8.03	7.76	7.70	177	108	94
Day 161	PAO	3	3	8.02	7.93	7.79	180	135	105
Day 161	PAO	6	1	8.03	7.82	7.76	235	184	152
Day 161	PAO	6	2	8.01	7.81	7.75	195	160	138
Day 161	PAO	6	3	7.93	7.79	7.67	185	139	115
Day 161	AQM	2	1	8.06	7.91	7.88	160	117	60
Day 161	AQM	2	2	7.92	7.87	7.81	214	204	151
Day 161	AQM	2	3	8.04	7.86	7.71	285	200	169
Day 161	AQM	7	1	7.94	7.79	7.76	185	141	-222

Day 161	AQM	7	2	8.01	7.79	7.69	175	137	105
Day 161	AQM	7	3	8.00	7.93	7.80	205	141	122
Day 161	PTF	4	1	7.84	7.72	7.68	-84	-141	-165
Day 161	PTF	4	2	8.02	8.05	7.70	-119	-147	-158
Day 161	PTF	4	3	7.77	7.75	7.69	-106	-146	-163
Day 161	PTF	1	1	7.86	7.77	7.73	-81	-112	-121
Day 161	PTF	1	2	8.00	7.81	7.75	-66	-120	-131
Day 161	PTF	1	3	7.61	7.64	7.63	-96	-155	-164

Table AI.2. Total wet weight, water content, concentration and concentration ratios of barium and drilling fluids in all sediment samples.

Sample	Ch. no.	Sample wet wght.	Water %	Barium mg.kg-1	Barium mg.cm-2	Drilling fluid mg.kg-1	Drilling fluid mg.cm-2	DF:Ba ratio
Cuttings samples								
PAO				41 000		56 300		1.373
AQM				50 000		115 766		2.315
PTF				51 000		60 500		1.186
Day 2								
PTF		33.18	59.27	8 300	8.406	16 528	18.525	2.204
PTF	4b	22.09	56.91	7 300	7.699	11 087	13.132	1.706
PTF	1a	27.35	62.44	8 200	7.566	17 331	17.720	2.342
PTF	1b	26.78	62.06	8 400	7.686	16 409	16.594	2.159
AQM	2a	27.73	56.25	6 300	6.640	10 100	12.193	1.836
AQM	2b	28.16	55.86	6 300	6.804	11 300	13.980	2.055
AQM	7a	26.53	55.48	8 300	8.814	15 000	17.628	2.000
AQM	7b	27.62	55.23	5 600	5.909	9 960	12.260	2.075
PAO	6a	26.87	61.48	5 600	4.944	6 302	6.491	1.313
PAO	6b	25.78	59.49	5 200	4.572	6 261	6.506	1.423
PAO	3a	26.60	64.05	6 900	5.806	11 027	10.495	1.808
PAO	3b	25.43	63.90	6 700	5.391	10 255	9.370	1.738
CON	5	25.87	62.86	800	0.000	-	-	-
Day 62								
PTF	4a	27.84	55.77	7 000	7.599	7 617	9.336	1.229
PTF	1a	27.32	57.05	7 100	7.355	10 264	11.983	1.629
AQM	2a	27.76	56.62	6 700	7.071	11 900	14.262	2.017
AQM	7a	28.34	56.66	8 300	9.168	14 600	17.847	1.947
PAO	6a	27.54	57.79	4 500	4.280	4 248	4.914	1.148
PAO	3a	27.35	59.27	6 200	5.987	6 812	7.553	1.261
CON	8	26.12	59.70	820	0.021	-	-	-
Day 111								
	4a	21.76	55.21	7 100	7.638	5 101	6.185	0.810
PTF	1a	27.17	57.63	7 200	7.333	9 232	10.577	1.443
AQM	2a	31.43	57.52	7 500	8.903	9 940	13.208	1.484

AQM	7a	26.99	57.55	7 200	7.298	10 800	12.316	1.688
PAO	6a	27.43	58.55	4 300	3.960	3 941	4.459	1.126
PAO	3a	26.29	60.20	5 800	5.206	5 449	5.673	1.090
Day 161								
PTF	4a	26.62	59.85	8 000	7.660	2 793	2.971	0.388
PTF	4b	27.32	58.27	6 800	6.809	2 072	2.351	0.345
PTF	1a	25.86	62.08	7 700	6.734	7 862	7.673	1.139
PTF	1b	26.30	61.03	7 200	6.529	5 733	5.848	0.896
AQM	2a	28.32	56.80	6 300	6.696	8 130	9.898	1.478
AQM	2b	28.02	57.49	4 100	3.912	4 850	5.750	1.470
AQM	7a		58.60	6 800	7.037	9 590	11.247	1.598
AQM	7b	28.28	57.03	6 200	6.530	8 480	10.255	1.570
PAO	6a	27.24	59.72	4 400	3.931	3 727	4.069	1.035
PAO	6b	21.78	59.37	4 100	2.906	3 165	3.484	1.199
PAO	3a	27.11	60.91	5 700	5.169	5 440	5.738	1.110
PAO	3b	26.36	61.94	6 800	5.990	6 207	6.196	1.035
CON	5	25.17	60.63	810	0.010	-	-	-

Table AI.3. Sediment oxygen consumption determined in each chamber ($\mu molO_2.m^{-2}.h^{-1}$).

Date	Day	CON 5	CON 8	PAO 3	PAO 6	AQM 2	AQM 7	PTF 4	PTF 1
2.May	6	172	105	265	249	328	390	430	468
3.May	7	177	97	299	280	284	419	417	431
4.May	8	54	29	229	207	197	257	318	345
5.May	9	68	197	212	357	317	345	512	429
6.May	10	98	115	352	269	201	292	363	357
8.May	12	172	178	381	373	273		425	438
10.May	14	139	118	362	303	293	347	452	431
13.May	17	55	154	227	326	453	303	632	443
18.May	22	279	649	585	649	621	546	818	733
20.May	24	176	35	338	290	588	307	688	500
24.May	28	91	86	348	394	442	349	792	600
27.May	31	123	94	335	298	385	290	548	364
31.May	35	112	183	314	533	245	501	921	650
3.Jun	38	186	184	521	518	448	461	931	651
7.Jun	42	220	205	619	578	581	518	1068	804
9.Jun	44	184	155	504	440	459	454	1144	797
14.Jun	49	203	223	627	540	711	604	1429	888
17.Jun	52	304	174	771	680	604	596	1264	1112
21.Jun	56	327	312	786	865	792	770	1700	1032
24.Jun	59	202	185	646	464	389	499	1290	1082
27.Jun	62	90	171	423	495	565	458	919	1107
1.Jul	66	69	79	394	352	609	370	1701	867
5.Jul	70	179	201	526	508	717	668	1747	1471
8.Jul	73	216	384	605	463	424	676	1704	1650
12.Jul	77	206	263	608	597	685	653	2225	1713
15.Jul	80	156	222	598	519	578	503	2275	1456
19.Jul	84	213	266	644	594	501	601	2191	1960
22.Jul	87	201	235	524	568	555	548	2499	1776
26.Jul	91	191	238	513	588	649	511	2502	1507
29.Jul	94	129	152	485	504	578	502	2389	1827
2.Aug	98	-18	63	196	356		387	1705	1117
5.Aug	101	128	154	407	498	281	462	920	1444
9.Aug	105	158	167	564	563	167	620	1103	1300
12.Aug	108	27	68	282	299	42	302	1871	1074
18.Aug	114	89	88	389	507	427	503	1778	1164
23.Aug	118	142	210	514	603	501	617	2495	2240
26.Aug	122	124	209	487	546	493	655	2113	1821
30.Aug	126	122	197	427	400	508	573	2119	1677
2.Sep	129	254	229		610	507	728	2147	
6.Sep	133	168	204	564	551	563	697	2000	1857
9.Sep	136	71	84	290	232	299	542	1664	1442
13.Sep	139	150	234	479	607	466	694	2207	1749
16.Sep	143	250	227	765	868	570	707	2661	2102
20.Sep	147	299	345	642	984	690	811	2070	2229
23.Sep	150	75	204		692	511	502	1796	1671
27.Sep	154	98			456	126	620	1601	1388
30.Sep	157	79	174		730	548	490	1791	1539
4.Oct	161	61	112		423	391	465	1459	1288

APPENDIX II: SINTEF Industrial chemistry report on chemical analyses

SINTEF

SINTEF

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SINTEF REPORT

TITLE

Test on Degradation of Novadril II 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 Novasol II eicosane isomers, Aquamul ether, Petrofree ester and barium content in sediment samples.

KEYWORDS	ENGLISH	NORWEGIAN
GROUP 1	Chemistry	Kjemi
GROUP 2	Analysis	Analyse
SELECTED BY AUTHOR(S)	Polyalphaolefine	Polyalfaolefin
	Barium	Barium
	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.

"Novasol II" is a new drill mud type where alkane compounds are substitutes for base oil. Tests to investigate the degradability and environmental effects of cuttings from drilling with Novasol II have been performed at the NIVA Marine Research Station at Solbergstrand.

The chemical analyses of sediment samples with regard to the content of Novasol II alkane compounds and the content of barium have been performed by SINTEF Industrial Chemistry on request from Norwegian Institute for Water Research (NIVA).

The investigation also includes tests with Aquamul 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 Novasol II alkane compounds, Aquamul ether, Petrofree esters and the content of barium in the sediment samples.

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2. CHEMICAL ANALYSES - METHODS

2.1 ANALYTICAL PROCEDURE

2.1.1 Identity of Novasol II

A sample of Novasol II was available from M-I Drilling Fluids Co. The product specifications state that the liquid is a hydrogenated polyalphaolefin based chemical and consist of eicosane isomers. This is established in a letter from M-I Drilling Fluids Co. (James E. Friedheim) to Jon Rytter Hasle, Saga Petroleum dated 28 March 1994.

To confirm the chemical identity, a sample of the received Novasol II liquid was analysed by gas chromatography-mass spectrometry (GC/MS). The analysis confirmed that tne liquid Novasol II consists of saturated hydrocarbon compounds with the chemical formula $C_{20}H_{42}$

2.1.2 Work-up procedure Novasol II, Aquamul B II and Petrofree

Wet sediment samples weighing 15-20 g were homogenized and placed in a Soxhlet tube. Internal standards, n-C_{16} and n-C_{22} (Novasol), dioctylether (Aquamul) and ethyl stearate (Petrofree) 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.

2.1.3 Work-up procedure Barium

An aliquote of the wet homogenized sediment was weighed out for determination of the dry weight and dried for 48 hours at 105°C. After drying barium was analysed with x-ray.

2.1.4 Determination of Novasol II alkane content

The Novasol II liquid is a mixture of eicosane isomers. Quantitation was carried out by measuring the flame ionization detector response of the $C_{20}H_{42}$ area.The area was compared to the corresponding response of known amounts of the internal standards n-$C_{16}H_{34}$ alkane and n-$C_{22}H_{46}$ alkane.

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.

2.1.5 Determination of Aquamul ether content

The Aquamul B II liquid consists of one main compound, an alkyl ether, $C_{20}H_{42}O_2$ (SINTEF Report STF27 F94030) while the sediment samples received from the Aquamul 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 same conditions as for Novasol II (2.1.4).
Typical gas chromatograms are shown in Figure 3.2.

2.1.6. Determination of Petrofree ester content

The Petrofree ester is a mixture of five homologous fatty acid esters. The main component is 2-ethylhexyl dodecanoate (SINTEF Report STF27 F94030). 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 same conditions as for Novasol II (2.1.4).
Typical gas chromatograms are shown in Figure 3.3.

2.1.7. Determination of Barium content

The samples were dried, crushed, homogenized, mixed with wax and pressed as pellets for x-ray fluorescence analysis. Reference material of known concentration of barium was used for standardization.

The samples were measured in vacuum at an angel 2 theta = 87,200, corresponding to Ba Lα1, with a LIF 100 crystal.

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

Novasol II
Two internal standards, n-$C_{16}H_{34}$ alkane and n-$C_{22}H_{46}$ alkane were 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 Novasol II at 2500 ppm concentration level. An average recovery of 98% was obtained after work up and analysis of three replicate samples.

Aquamul B II
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 103% was obtained after work up and analysis of three replicate samples.

Petrofree
An internal standard etyl stearate 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 Petrofree ester at 100 ppm concentration level. An average recovery of 95% was obtained after work up and analysis of three replicate samples.

2.2.3 Reproducibility

Novasol II
The reproducibility of the analytical procedure was determined by analyses of sediment samples spiked with known amounts of Novasol II. From three replicate sediments samples spiked with Novasol II a relative standard deviation of 0,8% was obtained for the determination of the eicosane isomers.

The reproducibility of the instrumental analysis (GC) of Novasol II was determined by analysing a standard solution consisting of Novasol II and the internal standards. The Novasol II standard was analysed together with the 13 samples. Two Novasol standards were analysed

followed by 6 samples, then one standard, the remaining 7 samples and one standard followed. This gave a total of four Novasol standards. The relative standard deviation between the 4 analysed Novasol standards was 1,4%.

Aquamul B II
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 4,7% 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 13 samples. Two Aquamul standards were analysed followed by the 13 samples and then two standards. This gave a total of four Aquamul standards. The relative standard deviation between the four analysed Aquamul standards was 0,2% for Aquamul II B and 2,8% for Aquamul B.

Petrofree
The reproducibility of the analytical procedure was determined by analyses of sediment samples spiked with known amounts of Petrofree ester. From three replicate sediments samples spiked with Petrofree ester a relative standard deviation of 0,4% was obtained for the ester determination.

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 13 samples. Two Petrofree standards were analysed followed by the 13 samples and then two standards. This gave a total of four Petrofree standards. The relative standard deviation between the four analysed Petrofree standards was 10%.

Barium
The relative standard deviation for the determination of barium with x-ray is estimated to 3%.

2.2.4 Quantitation limit

Novasol II
In these experiments the quantitation limit for Novasol II was set to 50 mg/ kg dry sediment.

Aquamul BII
In these experiments the quantitation limit for Aquamul B II was set to 10 mg/kg dry sediment. For Aquamul B the quantitation limit will be approximately 100 mg/kg dry sediment.

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

3 RESULTS AND DISCUSSION

3.1 Novasol II

3.1.1 Content of Novasol II eicosane isomers and barium in sediments from the Novasol II trays

The results from the analyses of the content of Novasol II eicosane isomers and barium in sediment samples collected in the two Novasol II trays are given in Table 2.1 and Table 2.2. Table 2.1 gives the results of the content of Novasol II in the sediments. Table 2.2 gives the results of the barium content in the same sediment samples.

Figure 2.1 shows a gas chromatogram of a mixture of Novasol II spiked with n-$C_{16}H_{34}$ alkane and n-$C_{22}H_{46}$ alkane (internal standards) together with gas chromatograms of Novasol II sediments extracts from day 2, day 62, day 111, day 161 and a control sample from day 2.

At intervals (day 2, 62, 111 and 161) samples were taken for Novasol II and barium analyses. The samples were collected at random. At day 2 and day 161 two replicate samples were taken from each of the two Novasol II trays. At day 62 and day 111 one sample was taken from each of the two Novasol II trays.

The contents of Novasol II eicosane isomers and barium were analysed in the cuttings sample used in the Novasol II trays:

The content of Novasol II was	56300 mg/kg dry cuttings.
The content of barium was	41000 mg/kg dry cuttings

The contents of Novasol II and barium were analysed in the control sample marked "Control-5 28/4-94:

Novasol II was not detected in the control sample	(< 50 mg/kg dry sediment).
The content of barium was	800 mg/kg dry sediment.

3.1.2 Discussion

In the present study the Novasol II mud liquid consists of eicosane isomers. A suitable analytical programme was set out to take care of these compounds. The procedure includes extraction 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 internal standards added to the sediments prior to work up.

The analytical procedure worked quite well. For spiked samples at a concentration of 2500 ppm Novasol II, 98% of the real value was found, and the relative standard deviation of three replicates was 0,8%.

The results from both the Novasol II trays listed in Table 3.1 show that a pronounced reduction in the Novasol II content has taken place from day 2 to day 161. The concentration of the Novasol II eicosane isomers is almost reduced by a factor of 2 in both trays.

Barium and Novasol II were analysed in the same sediment samples. An aliquote of the wet homogenized sediment was weighed out for determination of the dry weight and the content of

barium. The relative standard deviation for the determination of barium with x-ray is estimated to 3%.

The results from the analyses of barium are also listed in Table 3.1. The results show no change in the concentration of barium from day 2 to day 161 in tray 3. In tray 6 the mean value from day 161 is somewhat lower than the mean value from day 2. This is most probably due to inhomogeneity in the sample material since there is no reasonable explanation for a reduction in the barium content during this period of time.

The conclusion is that a reduction has taken place in the content of Novasol II, while no reduction is observed for the content of barium in the sediment samples from the Novasol II trays.

The main reduction of the Novasol II content took place in the period from day 2 to day 62.

Table 3.1

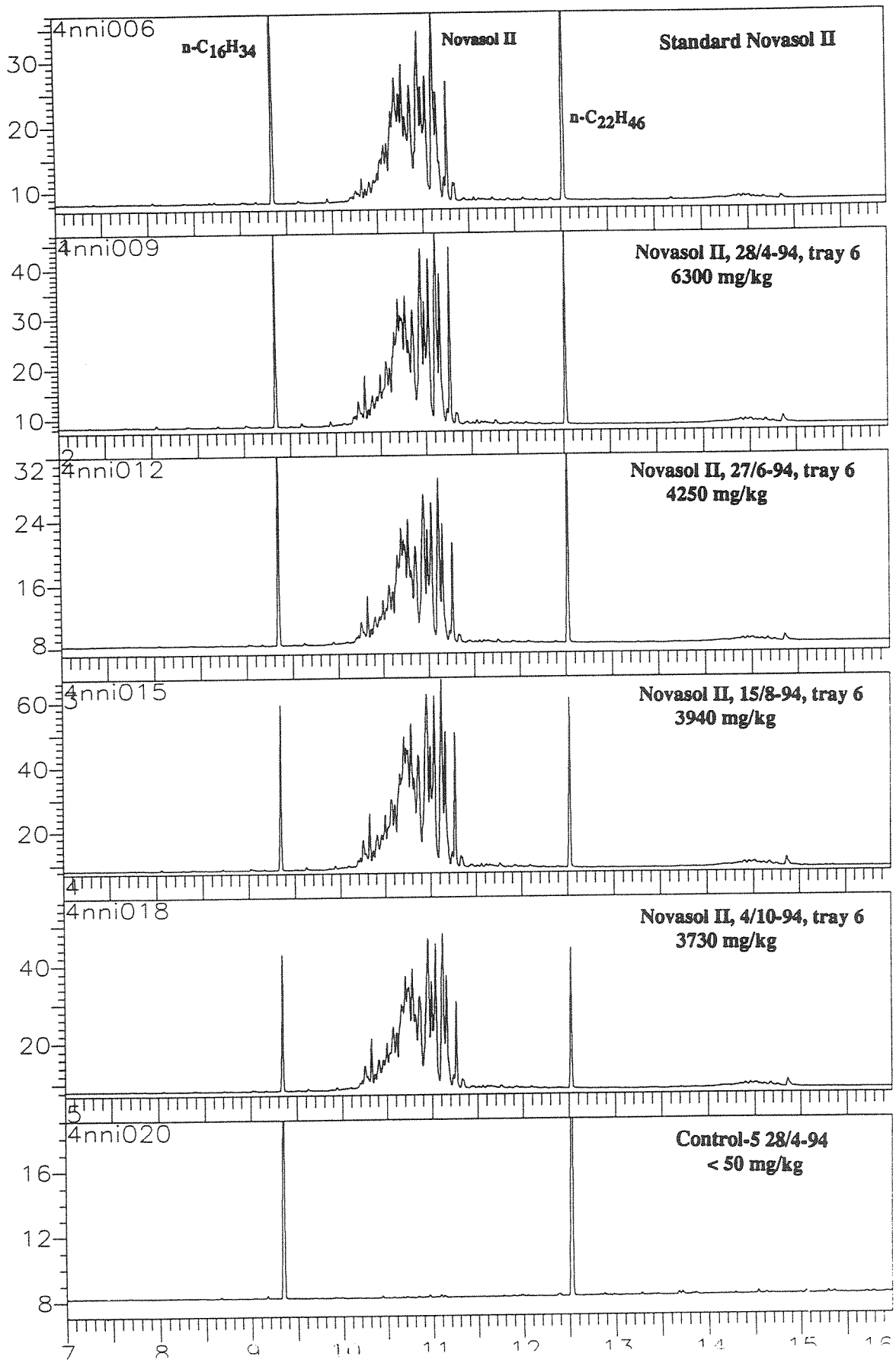
CONTENT OF NOVASOL II IN SEDIMENTS
(mg/kg dry sediment)

Sample	Box no.	Day 2 1994-04-28	Day 62 1994-06-27	Day 111 1994-08-15	Day 161 1994-10-04
Sediment from Novasol II trays	3	11000	6810	5450	5440
		10300			6210
mean		**10700**			**5830**
	6	6300	4250	3940	3730
		6260			3170
mean		**6280**			**3450**
Control	5	< 50			

CONTENT OF BARIUM IN SEDIMENTS
(mg/kg dry sediment)

Sample	Box no.	Day 2 1994-04-28	Day 62 1994-06-27	Day 111 1994-08-15	Day 161 1994-10-04
Sediment from Novasol II trays	3	6900	6200	5800	5700
		6700			6800
mean		**6800**			**6250**
	6	5600	4500	4300	4400
		5200			4100
mean		**5400**			**4250**
Control	5	800			

Figure 3.1
Gas chromatograms of Novasol sediment extracts from day 2, day 62, day 111 and day 161 together with a control sample and a standard of Novasol II eicosane isomers. The alkanes n-$C_{16}H_{34}$ and n-$C_{22}H_{46}$ is added as internal standards.



3.2 AQUAMUL ETHER

3.2.1 Content of Aquamul ether and barium 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 3.2. Both the separate results of the content of Aquamul B II and Aquamul B and the sum of Aquamul B II and Aquamul B content in the sediments are given. The content of barium in the sediment samples is also given in Table 3.2.

Figure 3.2 shows 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 2, day 62, day 111, day 161 and a control sample from day 161.

At intervals (day 2, 62, 111 and 161) samples were taken for Aquamul and barium analyses. The samples were collected at random. At day 2 and day 161 two replicate samples were taken from each of the two Aquamul trays. At day 62 and day 111 one sample was taken from each of the two Aquamul trays.

The content of Aquamul B II, Aquamul B and barium were analysed in the cuttings sample used in the Aquamul trays:

The content of Aquamul B II/ Aquamul B was	91800/24000 mg/kg dry cuttings.
The content of barium was	50000 mg/kg dry cuttings

The content of Aquamul and barium were analysed in the control sample marked "Control-5 4/10-94:

Aquamul was not detected in the control sample	(< 10/100 mg/kg dry sediment).
The content of barium was	810 mg/kg dry sediment.

3.2.2 Discussion

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 extraction 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, 103% of the real value was found, and the relative standard deviation of three replicates was 4,5 %.

The results from both the Aquamul trays listed in Table 3.2 show that a reduction in the Aquamul content has taken place from day 2 to day 161. The concentration of sum Aquamul B II and Aquamul B are reduced to 61% in tray no. 2 and to 72% in tray no. 7. Compared to Aquamul B II the reduction of Aquamul B is somewhat higher.

Barium and Aquamul were analysed in the same sediment samples. An aliquote of the wet homogenized sediment was weighed out for determination of the dry weight and the content of barium. The relative standard deviation for the determination of barium with x-ray is estimated to 3%.

The results from the analyses of barium are listed in Table 3.2 The results show no change in the concentration of barium from day 2 to day 161 in the two Aquamul trays

The conclusion is that a reduction has taken place in the content of both Aquamul B II and Aquamul B, while no reduction is observed for the content of barium in the sediment samples from the Aquamul trays.

Table 3.2

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

Sample	Box no.	Day 2 1994-04-28 Aqu B II/ Aqu B	Day 62 1994-06-27 Aqu B II/ Aqu B	Day 111 1994-08-15 Aqu B II/ Aqu B	Day 161 1994-10-04 Aqu B II/ Aqu B
Sediment from Aquamul trays	2	7950/2090 8900/2350	9760/2140	8230/1710	6850/1280 4180/675
mean		**8430/2220**			**5520/978**
	7	11900/3100 7910/2050	11900/2690	9060/1770	8210/1380 7170/1310
mean		**9910/2580**			**7690/1350**
Control	5				< 10/100

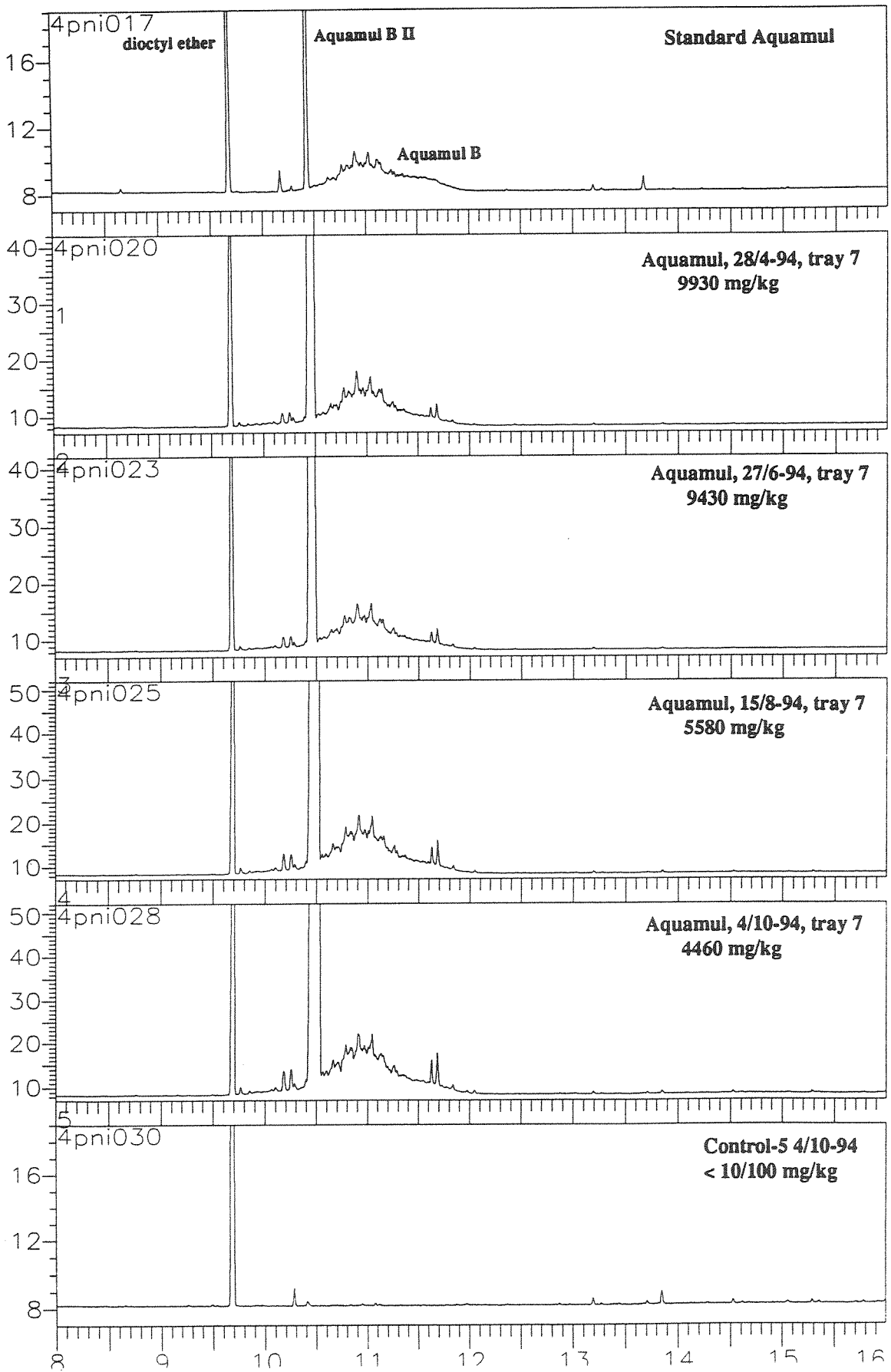
CONTENT OF SUM AQUAMUL B II AND AQUAMUL B ETHER IN SEDIMENTS
(mg/kg dry sediment)

Sample	Box no.	Day 2 1994-04-28	Day 62 1994-06-27	Day 111 1994-08-15	Day 161 1994-10-04
Sediment from Aquamul trays	2	10000 11300	11900	9940	8130 4850
mean		**10700**			**6490**
	7	15000 9960	14600	10800	9590 8480
mean		**12500**			**9040**
Control	5				< 10/100

CONTENT OF BARIUM IN SEDIMENTS
(mg/kg dry sediment)

Sample	Box no.	Day 2 1994-04-28	Day 62 1994-06-27	Day 111 1994-08-15	Day 161 1994-10-04
Sediment from Aquamul trays	3	6300 6300	6700	7500	6300 4100
mean		**6300**			**5200**
	6	8300 5600	8300	7200	6800 6200
mean		**6950**			**6500**
Control	5				810

Figure 3.2
Gas chromatograms of Aquamul sediment extracts from day 2, day 62, day 111 and day 161 together with a control sample and a standard of Aquamul ether (mixture of Aquamul B II and Aquamul B drilling fluid). Dioctyl ether is added as internal standard.



3.3 PETROFREE ESTER

3.3.1. Content of Petrofree ester and Barium 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 3.3. The content of barium in the sediment samples is also given in Table 3.3

Figure 3.3 shows a gas chromatogram of Petrofree ester standard spiked with ethyl stearate (internal standard) together with gas chromatograms of Petrofree sediments extracts from day 2, day 62, day 111, day 161 and a control sample from day 62.

At intervals (day 2, 62, 111 and 161) samples were taken for Petrofree and barium analyses. The samples were collected at random. At day 2 and day 161 two replicate samples were taken from each of the two Petrofree trays. At day 62 and day 111 one sample was taken from each of the two Petrofree trays.

The content of Petrofree ester and barium were analysed in the cuttings sample used in the Petrofree trays:

The content of Petrofree ester was	60500 mg/kg dry cuttings.
The content of barium was	51000 mg/kg dry cuttings

The content of Aquamul and barium were analysed in the control sample marked "Control-8 27/6-94:

Aquamul was not detected in the control sample	(< 2 mg/kg dry sediment).
The content of barium was	820 mg/kg dry sediment.

3.3.2 Discussion

In the present study the Petrofree mud liquid consists of fatty acid esters. A suitable analytical programme was set out to take care of these ester compounds. The procedure includes extraction 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 100 ppm Petrofree ester, 95% of the real value was found, and the relative standard deviation of three replicates was 0,4 %.

The results from both the Petrofree trays listed in Table 3.3 show that a pronounced reduction in the Petrofree ester content has taken place from day 2 to day 161. The concentration of Petrofree ester in tray 1 is reduced by a factor of 2, while the concentration of Petrofree ester in tray 4 is reduced by a factor of 5.

Barium and Petrofree ester were analysed in the same sediment samples. An aliquote of the wet homogenized sediment was weighed out for determination of the dry weight and the content of barium. The relative standard deviation for the determination of barium with x-ray is estimated to 3%.

The results from the analyses of barium are listed in Table 3.3 The results show no change in the concentration of barium from day 2 to day 161 in none of the two Petrofree trays.

The conclusion is that a reduction has taken place in the content of Petrofree ester, while no reduction is observed for the content of barium in the sediment samples from the Petrofree trays.

There is also observed that the reduction of Petrofree ester is more pronounced than the reduction of both Novasol eicosane isomers and Aquamul eter.

3.4 Barium

The content of barium in the three different cuttings samples varied from 41000 (Novasol) to 51000 mg /kg dry cuttings. The concentration of barium in the three control samples varied between 800 to 820 mg/kg dry sediment.

The results from the analyses of barium in the sediment trays show no change in the concentration of barium during the experimental period from day 2 to day 161. The minor variation in the content of barium in the sediment trays is most probably due to inhomogeneity in the sample material.

Table 3.3

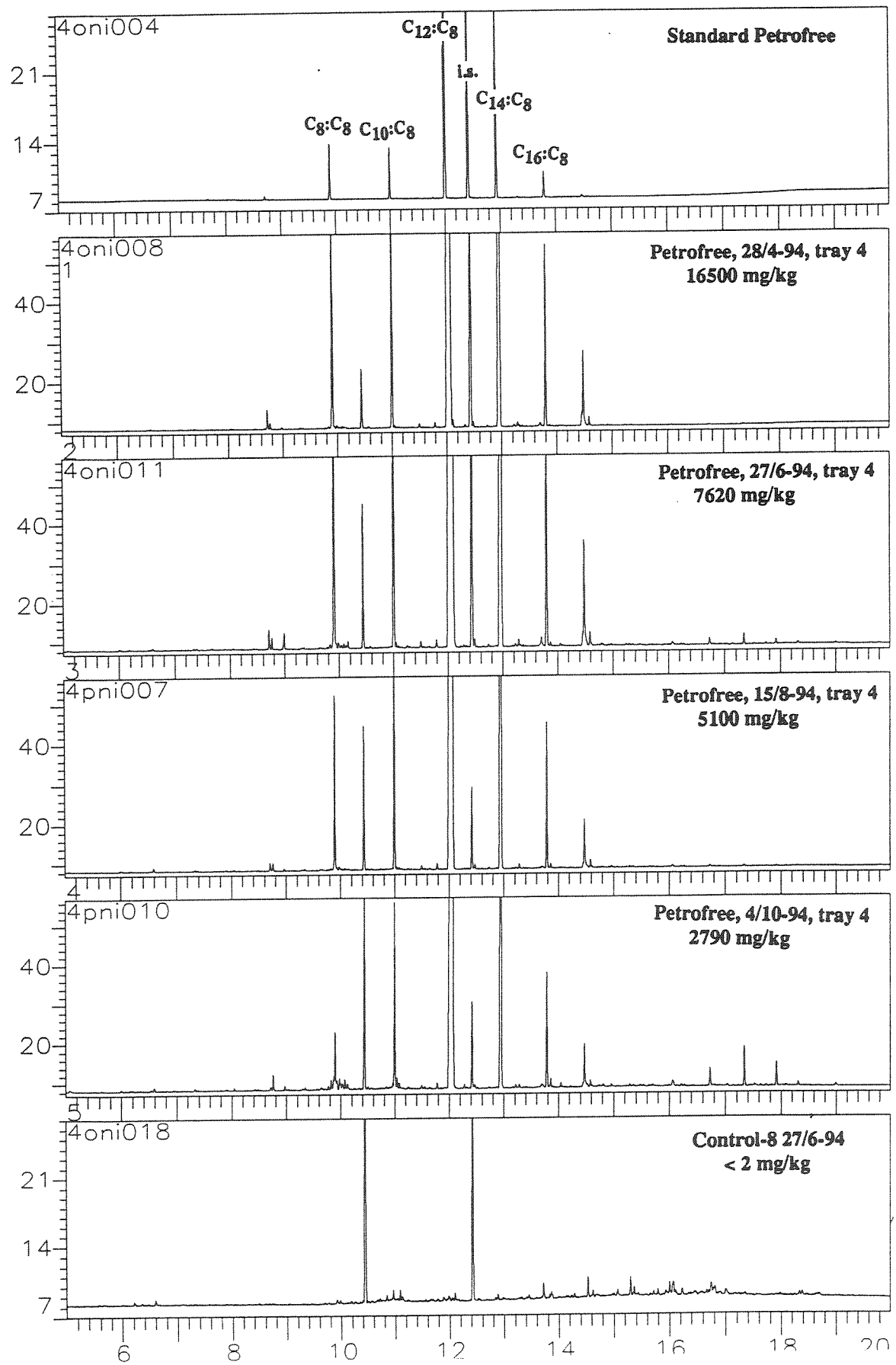
CONTENT OF PETROFREE ESTER IN SEDIMENTS
(mg/kg dry sediment)

Sample	Box no.	Day 2 1994-04-28	Day 62 1994-06-27	Day 111 1994-08-15	Day 161 1994-10-04
Sediment from Petrofree trays	1	17300	10300	9230	7860
		16400			5730
mean		**16900**			**6800**
	4	16500	7620	5100	2790
		11100			2070
mean		**13800**			**2430**
Control	8		< 2		

CONTENT OF BARIUM IN SEDIMENTS
(mg/kg dry sediment)

Sample	Box no.	Day 2 1994-04-28	Day 62 1994-06-27	Day 111 1994-08-15	Day 161 1994-10-04
Sediment from Petrofree trays	1	8200	7100	7200	7700
		8400			7200
mean		**8300**			**7500**
	4	8300	7000	7100	8000
		7300			6800
mean		**7800**			**7400**
Control	8		820		

Figure 3.3
Gas chromatograms of Petrofree sediment extracts from day 2, day 62, day 111 and day 161 together with a control sample and a standard of Petrofree ester. Ethyl stearate is added as internal standard.



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