02-3321

O-94241 O-95100

Biodegradation of Ultidril Base Fluid and Drilling Mud on Cuttings Deposited in Benthic Chambers

NIVA - REPORT

Report No.:	Sub-No.:
O-94241, O-95100	
Serial No.:	Limited distrib.:
3321	

Norwegian Institute for Water Research NIVA

Main Office	Regional Office, Sørlandet	Regional Office, Østlandet	Regional Office, Vestlandet	Akvaplan-NIVA A/S
P.O. Box 173, Kjelsås	Televeien 1	Rute 866	Thormøhlensgt 55	Søndre Tollbugate 3
N-0411 Oslo	N-4890 Grimstad	N-2312 Ottestad	N-5008 Bergen	N-9000 Tromsø
Norway	Norway	Norway	Norway	Norway
Phone (47) 22 18 51 00	Phone (47) 37 04 30 33	Phone (47) 62 57 64 00	Phone (47) 55 32 56 40	Phone (47) 77 68 52 80
Telefax (47) 22 18 52 00	Telefax (47) 37 04 45 13	Telefax (47) 62 57 66 53	Telefax (47) 55 32 88 33	Telefax (47) 77 68 05 09

Report Title:	Date:	Printed:
Biodegradation of Ultidril Base Fluid and Drilling Mud on Cuttings Deposited in Benthic Chambers	27.09.95	NIVA 1995
	Topic group: Oil and Gas	
Author(s): Morten T. Schaanning	Geographical area: North Sea	
	Pages: 64+app	Edition:

Client(s):	Client ref.:
Elf Petroleum Norge as, Schlumberger Dowell IDF.	

Abstract:

Synthetic drilling fluids have replaced much of the mineral oil previously used in mud systems for offshore 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 a new olefin base fluid were deposited on marine sediments in continuously flushed benthic chambers. Replicate chambers were treated with Ultidril, Petrofree and Novasol II base fluids and cuttings and non-contaminated control sediments. By the end of the experimental period, oxygen consumption could account for complete conversion of 23-80% of the added drilling fluid carbon to CO_2. 0.5-38% remained present in the sediment. Half-lives ranged from 20 days for Petrofree ester, 43 days for Ultidril olefins and 127 days for Novasol II. Effects on redox potentials and macrobenthtic communities were inversely related to the half-life of the drilling fluids. However, sulphide toxicity of the pore water was only observed in the chamber treated with Petrofree ester.

4 keywords, Norwegian

1. oljeboring
2. kjemikalier
3. miljøeffekter
4. sedimenter

4 keywords, English

1. oil drilling
2. chemicals
3. environmental effects
4. sediments

Project manager

Morten T. Schaanning

For the Administration

Torgeir Bakke

ISBN82-577-2847-0

Norwegian Institute for Water Research

O-94241/O-95100

Biodegradation of Ultidril Base Fluid and Drilling Mud on Cuttings Deposited in Benthic Chambers

Project manager:	Morten T. Schaanning
Co-workers:	Oddbjørn Pettersen
	Einar Johansen
	Håkon Oen
	John Arthur Berge
Sub-contracted:	Frøydis Oreld and Ingegerd Rustad, SINTEF-Industrial Chemistry
	Sabine Cochrane and Rune Palerud, Akvaplan-niva,
	Anders Warén, Naturhistoriska Riksmuseet, Stockholm
Quality Assurance:	Torgeir Bakke, NIVA-Oslo

1. SUMMARY 7

2. INTRODUCTION 19

3. MATERIAL AND METHODS 21

3.1 TEST SET-UP AND ENVIRONMENTAL CONDITIONS 21

3.2 ADDITION OF CUTTINGS 24

3.3 SAMPLING AND ANALYTICAL METHODS 25
3.3.1 Sediment samples 25
3.3.2 Sample work-up and concentration units 27
3.3.3 Oxygen consumption 28
3.3.4 Electrode measurements 29
3.3.5 Reproducibility of pH and E_h measurements 30

4. RESULTS AND DISCUSSION 31

4.1 DRILLING FLUIDS AND BARIUM 31
4.1.1 Recovery of the cuttings added 31
4.1.2 Loss during the test period 34
4.1.3 Chemical structure and relative degradability of Ultidril components 40

4.2 OXYGEN CONSUMPTION 41

4.3 MASS BALANCE OF DRILLING FLUIDS 46

4.4 EFFECTS OF ADDITION OF CUTTINGS 48
4.4.1 Visual effects 48
4.4.2 pH and redox potential deviations 51
4.4.3 Composition of benthic communities by the end of the experiment 56

5. CONCLUSIONS 59

6. REFERENCES 63

7. APPENDIX I: TABLES OF RESULTS 65

8. APPENDIX II: ANALYSES OF BENTHIC FAUNA FROM EXPERIMENTAL TANKS AT SOLBERGSTRAND, AKVAPLAN-NIVA 73

9. APPENDIX III: REPORT ON CHEMICAL ANALYSES, SINTEF-INDUSTRIAL CHEMISTRY 77

Preface

This report describes the results of NIVA projects O-94241 and O-95100. Project O-94241 on biodegradation and biogeochemical effects in benthic chambers treated with Ultidril was performed for Elf Petroleum Norge AS on request from SFT. Project O-95100 on the benthic fauna was funded by Schlumberger Dowell IDF. The experimental work was done at NIVA Marine Research Station Solbergstrand (MFS) during the period November 1994 - May 1995. SINTEF Industrial Chemistry was subcontracted to perform the chemical analyses of drilling fluids and barium. Their report is enclosed in Appendix III. Akvaplan-niva was subcontracted for sorting the biological samples and identification of appropriate taxonomic groups. Molluscs were sent forward for identification by Anders Warèn, Naturhistoriska Riksmuseet, Stockholm.

Oslo, September 27, 1995

Morten T. Schaanning
Project Manager

1. 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 less than about 5 km from the discharge site.

Three types of synthetic drilling fluids are currently in use. ***Ester*** and ***ether*** compounds are characterised 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 more rapidly 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 initiated by an initial enzymatic cleavage of carbon-carbon double bonds. Previous investigations have shown that biodegradation of hydrogenated polyalphaolefin base fluids, which did not have any double bond, occurred at rates comparable to the biodegradation of ether and mineral oil base fluids.

The present test object was a new type of olefin base fluid, which is produced by *Schlumberger Dowell IDF* and marketed under the trade name *Ultidril*. Information from the manufacturer stated that Ultidril base fluid was a hexadecene in a mixture with some tetra- and octadecene. GC-MS analyses performed by SINTEF Industrial Chemistry on the base fluid sample used in the present experiment, confirmed that the base fluid consisted of a mixture of tetradecene with the chemical formula $C_{14}H_{28}$ and hexadecene with the chemical formula $C_{16}H_{32}$.

The objectives of the present investigation was to assess the environmental fate of this new mud system after its` deposition on the seabed as compared to the fate of previously tested ester and olefin base fluids on cuttings. The reference ester delivered

from Baroid under the trade name Petrofree was 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 reference polyalphaolefin delivered from MI under the trade name Novasol II, was a saturated hydrocarbon with the chemical formula $C_{20}H_{42}$.

The assessment was based on a six months benthic chamber experiment performed at the Marine Research Station Solbergstrand (MFS), which is situated by the Oslofjord south of the sill at Drøbak.

Test set-up and sampling strategy

All cuttings were sampled from recent drilling operations in the North Sea. The Ultidril cuttings were sampled at the Frøy platform and arrived at NIVA in October 1994 along with a small sample of Ultidril base fluid proper. Both reference cuttings were delivered to NIVA in February 1994. Subsamples of the reference cuttings which contained Novadril II and Petrofree muds, respectively, had been used in a previous test (NIVA Report No 3178).

The experiment comprised eight identical, transparent acrylic chambers. Each chamber measured 0.5x0.5x0.4m and was filled with a 25 cm layer of sediment and a 15 cm layer of seawater. The 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 6-10°C and 33.5-34.5 PSU, respectively.

On day zero, aliquots of the cuttings samples were diluted with non-contaminated control sediment and suspended in a small volume of seawater to produce a slurry which was added to the chamber water. Thus, similar amounts of particles were allowed to settle in an approximately one millimetre thin layer on top of the sediment in each chamber.

Two chambers were treated with control sediment soaked with Ultidril base fluids and another two chambers were treated with Ultidril cuttings from the Frøy platform. For reference purposes, one chamber was treated with Petrofree cuttings and another chamber was treated with Novadril II cuttings, both sampled from off-shore drilling

operations. The two remaining chambers were treated with non-contaminated control sediments.

The addition was done on November 15th, 1994. During the next six months, the chambers were sampled for various purpose and parameters at various time intervals. Thus, chemical analyses of drilling fluids and barium was determined in sediment samples collected 3, 27, 62, 100, 160 and 176 days after addition. At the same time intervals, visible changes on the sediment surfaces were noted and pH and redox potentials were determined at 5, 15 and 25 mm depth at three different locations in each chamber. Oxygen consumption was determined twice a week by measuring the flow of water through each chamber and the difference in oxygen concentration between in- and outlet. After termination of the experiment (day 177), the macrofauna in the 0-10 cm top layer was sampled by washing the sediment on a one millimetre mesh size sieve.

Recovery of added drilling fluids and barium on day 3

Compared to the amounts added with the respective slurries, 70.0-97.1% of the barium and 57.1-90.8% of the drilling fluids were recovered on the sediment surface of the various chambers on day 3. The fact that the ratio between drilling fluids and barium observed in the sediment on day 3 was very similar to the ratio found in the cuttings samples showed that the drilling fluids were strongly attached to particles in the added slurries and that the moderate loss of drilling fluids and barium during set-up of the experiment, most probably had resulted from cuttings particles being washed out of the chambers when the water flow was initiated on day one after addition of the slurries to the chamber water.

Loss of barium during experimental period

During the experimental period between the initial sampling on day 3 and the final sampling on day 176, any loss of drilling fluids attached to cuttings particles should be revealed by a corresponding loss of barium. In three of the four chambers treated with cuttings, linear regression analyses on the concentration of barium showed no significant change during the experimental period. A significant decrease of the concentration of barium in the sediment samples was observed in the fourth chamber. However, this decrease was concluded to be an artefact of non-representative sampling of the cuttings layer, rather than from a real loss of cuttings particles. Thus, no loss of

particles from the chambers were found to occur during the experimental period between the initial and final sample collection.

Loss of drilling fluids

Sediment samples collected three days after addition of cuttings revealed initial concentrations of 1.7-3.4 mg DF·cm^{-2}. In previous tests initial concentrations have ranged 3.2-17.9 mg DF·cm^{-2}. Compared to concentrations found around off-shore installations the initial concentration corresponded to concentrations of mineral oil frequently found up to a distance of 500 m from the discharge point.

During the experimental period the mean concentration of Ultidril olefins in the four chambers treated with cuttings and base fluids, decreased from 2.5-3.4 mg·cm^{-2} on day 3 to 0.1-0.3 mg·cm^{-2} on day 176. Novasol II olefins decreased from 1.7 mg·cm^{-2} on day 3 to 0.66 mg·cm^{-2} on day 176 and Petrofree esters decreased from 2.4 mg·cm^{-2} on day 3 to 0.01 mg·cm^{-2} on day 176. Thus, by the end of the experiment, 38% of the Novasol II olefins, 3-10% of the Ultidril olefins and 0.5% of the Petrofree esters remained present in the sediment.

Similarly, the ratio between the concentrations of drilling fluids and barium in the Novadril chamber decreased from 1.00 on day 3 to 0.54 on day 176. In the Petrofree chamber, the ratio decreased from 1.34 on day 3 to 0.005 on day 176, and in the two chambers treated with Ultidril cuttings, the ratio decreased from 0.97-0.99 on day 3 to 0.072-0.079 on day 176. Furthermore, whereas the ratio decreased throughout the experimental period in the Ultidril and Petrofree chambers no decrease was observed in the Novadril chamber after day 100.

The half-life of the drilling fluid in each chamber, was calculated from curve equations obtained by fitting the observed change of concentration to a first order reaction model. Thus, in the six chambers treated with drilling fluids, exponential regression analyses gave correlation coefficients, r, between 0.947 and 0.976. This showed that in all chambers, the decrease of drilling fluids was significant at a 95% confidence level. The half-lives calculated from the curve equations were 36.0-49.9 days for the two chambers treated with Ultidril cuttings and 38.5-45.8 days for the two chambers treated with Ultidril base fluids. Thus, the half-life of the Ultidril base fluid appeared to be independent on whether the chamber was treated with base fluid proper or base fluid in cuttings sampled from an off-shore drilling operation.

The mean half-life of Ultidril was 42.6 days. This was intermediate between the 19.6 days found for the Petrofree esters and 127 days for the Novasol II olefins. Unfortunately, the half-life is not independent on the initial concentration. Strictly then, the half-lives of 19.6 and 127 days apply only to initial concentrations of 2.4 and 1.7 $mg \cdot cm^{-2}$, respectively. In previous tests, a half-life of 20 days has been found for Petrofree esters at an initial concentration of 4.2 $mg \cdot cm^{-2}$, and a half-life of 207 days has been found for Novasol II at initial concentrations between 6.3 and 9.9 $mg \cdot cm^{-2}$. Thus, taking different initial concentrations into consideration, the half-lives of both reference fluids determined in the present test were in good agreement with those determined in previous tests.

The GC/MS analyses revealed that the Ultidril base fluid was composed of a mixture of C_{14} and C_{16} olefins. It is frequently assumed that the length of the carbon chain will influence on the rate of biodegradation. In the present study the peak-areas for C_{14} and C_{16} olefins were determined separately from the Ultidril chromatograms. The fact that the C_{14}:C_{16} peak-area-ratio decreased throughout the experimental period, from 1.8 on day 3 to 0.61 on day 176, confirmed that the C_{14}-olefins degraded faster than the C_{16}-olefins.

Sediment oxygen consumption

In both control chambers the mean rates (weighted) of the sediment oxygen consumption were 217 $\mu molO_2 \cdot m^{-2}h^{-1}$, for the entire experimental period. No clear time trends were found and the variation expressed as one standard deviation of the 45 observations in each chamber was 79 and 64 $\mu molO_2 \cdot m^{-2}h^{-1}$, respectively.

In the chamber treated with Novadril cuttings, the mean rate of oxygen consumption was 319 $\mu molO_2 \cdot m^{-2}h^{-1}$ for the 0-176 days period. However, oxygen consumption rates decreased after two to three months. Thus, for the 0-90 days period, the mean rate of oxygen consumption was 423 $\mu molO_2 \cdot m^{-2}h^{-1}$, and for the remaining 90-176 days period the mean rate was 207 $\mu molO_2 \cdot m^{-2}h^{-1}$, which was not significantly different from control rates. The absence of any net respiration during the last half of the experimental period was consistent with the slow loss of Novasol base fluid from the sediment samples and the absence of any decrease of the Novasol:Ba ratio during the 100-176 days period.

In the chamber treated with Petrofree cuttings, the rate of oxygen consumption increased from control level on day zero to a maximum rate of 1420 $\mu molO_2 \cdot m^{-2}h^{-1}$ on day 48. During the 48-70 days period the oxygen consumption decreased rapidly to

about 700 $\mu molO_2 \cdot m^{-2}h^{-1}$. After day 70, the rate decreased more slowly. By the end of the experiment, oxygen consumption in the chamber treated with Petrofree cuttings was still approximately twice as high as the oxygen consumption in the control chambers. The mean rate of oxygen consumption for the 0-176 days experimental period, was 760 $\mu molO_2 \cdot m^{-2}h^{-1}$ in the Petrofree chamber.

In the four chambers treated with Ultidril cuttings and Ultidril base fluid, the mean oxygen consumption for the entire period ranged between 593 and 628 $\mu molO_2 \cdot m^{-2}h^{-1}$. The peak of the oxygen consumption rates observed in the Petrofree chambers between day 0 and day 70, did not occur in the Ultidril chambers. During this period, the rates in the Ultidril chambers varied between 500 and 1000 $\mu molO_2 \cdot m^{-2}h^{-1}$ and the mean value of 680 $\mu molO_2 \cdot m^{-2}h^{-1}$ for the 0-90 days period was significantly less than the corresponding rate of 940 $\mu molO_2 \cdot m^{-2}h^{-1}$ observed in the Petrofree chamber. During the last 90-176 days period, the oxygen consumption of 528 $\mu molO_2 \cdot m^{-2}h^{-1}$ in the Ultidril chambers were not much different from the corresponding 566 $\mu molO_2 \cdot m^{-2}h^{-1}$ observed in the Petrofree chamber.

The peak of oxygen consumption which occurred in the Petrofree chamber 1-3 months after addition of cuttings, has been observed in all previous tests. Most probably, the peak result from rapid metabolisation of fatty acid and alcohol produced during an initial step of enzymatic hydrolyses of the ester bond.

Biodegradation of olefins is frequently assumed to begin with an attack on the carbon-carbon double bond and proceed with oxidation of carbon atoms one by one up the chain of the organic molecule. During the initial period oxygen consumption rates should increase as a result of adaptation of the microbial communities. Towards the end of the experiment the rates should decrease as a result of decreasing substrate availability. If the initial attack on the double bond is rate determining in the biodegradation process, the hydrogenated Novasol II base fluid should not stimulate bacterial activity to the same extent as should the Ultidril olefins. The lower maximum rates of oxygen consumption observed in the Novadril chamber as compared to the Ultidril chamber, showed the relevance of the double bond. Thus, different rates and trends of oxygen consumption in the chambers treated with Petrofree esters, Ultidril olefins and Novasol II hydrogenated olefins, confirmed the different molecular structure of the base fluids.

Mass balance

A mass balance of the drilling fluids was constructed for each separate chamber for the period 0-176 days. In this mass balance it was assumed that the difference between the amount of drilling fluids present in the sediment on day 3 and day 176 had been lost via particle relocation and biodegradation. Relocation of cuttings particles could be estimated from the loss of barium. Complete degradation of drilling fluid carbon to CO_2 was calculated from the oxygen consumption measurements. Any presence of partly degraded drilling fluids or leakage of soluble drilling fluids or degradation products to the watermass, might show up as a deficit in the mass balance.

The mass balance showed that of the drilling fluids present on day 3, 23-80% was accounted for by oxygen consumption and 0.5 -38% remained present in the sediments on day 176. No significant loss was found to occur via particle relocation, and the mass balance deficit varied between 20% and 46%. Of the observed loss, respiration could account for 80% of the Petrofree esters and 49-64% of the Ultidril olefins, but only 38% of the Novasol olefins.

By the time of the final sampling, oxygen consumption in the Petrofree and Ultidril chambers was still high compared to control chambers. Therefore, in a prolonged experiment, the respiration fraction might have continued to increase until, eventually, all drilling fluid carbon had been converted to CO_2. In the Novadril chamber, however, biodegradation appeared to have terminated at about day 100. Oxygen consumption had declined to a level similar to control chambers, and no further decline neither of the concentration of the base fluid nor the DF:Ba concentration ratio was observed. Thus, with regard to the Novasol II olefins, it appeared that a refractory fraction of considerable magnitude might remain present at the deposition sites for a period of time longer than the one predicted by the estimated half-life.

In a previous test, initial concentrations of Novadril olefins were higher and biodegradation had not terminated by the end of the experimental period, 161 days after deposition of the cuttings. By then, 60% of the added olefins remained present in the sediment and respiration could only account for 43% of the total loss. Thus, in both tests a large fraction of the added olefins remained present in the sediments throughout the test periods and complete mineralisation to CO_2 could account for less than 50% of the total loss.

Visual changes on sediment surface

Visual changes on the sediment surface were noted when the lids were removed on each sampling occasion.

Thus on day 3, the added material was seen present on top of the sediment as an approximately one millimetre thin layer. Numerous perturbations and tracks in the freshly deposited layer revealed the presence of an active macrofauna community.

The appearance of the surface layer in the two control chambers and the chamber treated with Novadril cuttings did not change much during the experiment.

In the Petrofree chamber, yellow and black spots were noted during inspection on day 27. On day 63 approximately 80% of the surface had turned black and some white spots had also occurred. Most of the black areas did, however, disappear during the 100-160 days period.

In the four chambers treated with Ultidril cuttings and base fluids, small yellow spots had occurred on the sediment surface on day 27. Black spots never developed in these chambers, but the yellow spots remained present until day 100.

Empty, white shells of a small mussel had appeared on the surface in some of the chambers on day 63. Towards the end of the experiment, brief counts showed that 3-9 shells had accumulated in the Ultidril chambers, 7 in the Petrofree chamber and 2 in each of the control and Novadril chamber.

Effects on pH

pH and redox potentials were measured on each sampling occasion in the overlying water and at 5, 15 and 25 mm depth at three different locations in the sediments in each chamber. Thus, on each sampling occasion six replicate observations at each depth in the two control chambers could be compared with six replicate observations in two chambers treated with Ultidril base fluids, six replicate observations in two chambers treated with Ultidril cuttings, three replicate observations in one chamber treated with Novadril cuttings and three replicate observations in one chamber treated with Petrofree cuttings. Multiple comparisons were performed for each sampling occasion as well as after grouping the entire time series, using the SYSTAT© statistical software for the Macintosh.

Significant difference between control and treated chambers was only found in the Petrofree chamber at 15 and 25 mm depth on day 104. The ΔpH (= treated - control) was -0.28 and -0.27 pH-units, at the two depths, respectively. Grouped for the entire time series, significant deviations were again found only at 15 and 25 mm depth in the Petrofree chamber. The mean ΔpH for the experimental period was -0.118 and -0.121 at those two depths, respectively.

In the two Ultidril treatments, mean ΔpH for the experimental period ranged between -0.058 and -0.064 pH-units at 15 and 25 mm depth, but p-values between 0.20 and 0.37 showed that these deviations were not significant. In the Novadril chamber mean ΔpH was -0.005 (p=1.00) and 0.026 (p=0.96) at 15 and 25 mm depth, respectively.

Thus, whereas the deposition of Novadril cuttings had no clear effect on the pH, Petrofree and Ultidril treatments produced small negative deviations at 15 and 25 mm depth in the sediments. However, only the lowering observed in the Petrofree chamber was significant at the 95% confidence level. All pH deviations were well within any limits set for biological effects in the marine environment.

Effects on redox potentials

In the chamber water the E_h ranged 267-355 mV. In the sediments the potentials decreased with increasing depth. Thus, in the control chambers the E_h decreased from 270-370 mV at 5 mm depth to 138-183 mV at 25 mm depth. The lowest values were observed in the Petrofree chamber, in which a minimum value of -131 mV was recorded on day 27 below a black area.

The statistical analyses showed significant deviations at all depths in the sediment in the Petrofree chamber on day 28 and 63 and at 5 mm and 15 mm depth on day 104. Those potentials were 101-237 mV lower than the potentials recorded at corresponding depths in the control chambers. In the other treatments, the only significant deviation was observed on day 28, at 15 mm depth in the chambers treated with Ultidril cuttings. This deviation was -84 mV and the corresponding p-value was 0.045.

For the entire time series, mean negative deviations were observed at all depths in all treatments. The deviations were 75-116 mV in the Petrofree treatment, 39-45 mV in the Ultidril base fluid treatment, 41-48 mV in the Ultidril cuttings treatment and 9-22 mV in the Novadril treatment. The deviations were significant at the 95% confidence level

in the Petrofree treatment ($p=0.000$) and both Ultidril treatments ($p\leq0.042$), but not in the Novadril treatment ($p\geq0.559$).

Thus, during the experimental period, the deposition of Novadril cuttings had no significant effect on neither pH nor redox potentials. Deposition of Petrofree cuttings, Ultidril cuttings and Ultidril base fluids produced significant lowering of the redox potentials in the sediment.

Macrofauna

The macrofauna samples were sorted into the main taxonomic groups, Polychaeta, Crustacea and Mollusca. The sorted samples were further identified to family or species level. Thus, 15 different taxa were identified and up to 446 individuals were found in each chamber. The chambers were dominated by high numbers of the polychaete *Nereis diversicolor* and the small snails *Hydrobia ulvae & ventrosa.*

Nereis diversicolor is known for high tolerance in low-oxic environments and rapid colonisation of areas with an increased supply of nutrients or digestible organic matter. During species identification, a remarkable difference between the size of the individuals in the various treatments was observed. Determination of mean biomass of polychaete individuals showed a variation from 11 mg in the control chambers to 31 mg in the Petrofree chamber. Linear regression analyses of biomass versus total oxygen consumption in each chamber showed significant correlation with a regression coefficient, r of 0.92.

Also, the correlation between oxygen consumption and total number of individuals of species other than the two dominant groups *Nereis* and *Hydrobia*, was significant with an r-value of 0.72. Correlation analyses between total number of individuals and oxygen consumption failed because of incomplete analyses of one of the control chambers and strong deviation of the number of dominant individuals in one chamber treated with Ultidril base fluids. Nevertheless, omitting these two chambers, the total number of individuals of 381-446 in the chambers treated with Petrofree esters and Ultidril olefins, was clearly higher than the 244-268 individuals found in the Novadril treatment and control. The fact that the total individual numbers in the Petrofree chamber (381) was slightly smaller than those found in the Ultidril chambers (412-446), was in fact consistent with the classical model which predicts a lowering of individual numbers in heavily overloaded environments.

Thus, the deposition of drilling fluids had affected the structure of the chamber communities in a way resembling the characteristic effects of organic enrichment, and opportunistic species had increased their growth in proportion to the energy released by biodegradation of the drilling fluids.

Conclusions

1. GC/MS-analyses confirmed that the supplied sample of liquid Ultidril base fluid was a mixture of two unsaturated olefin compounds with the chemical formulae $C_{14}H_{28}$ and $C_{16}H_{32}$.
2. Negligible differences were found between chambers treated with Ultidril mud on cuttings sampled from off-shore drilling operations and chambers treated with non-contaminated sediment soaked with Ultidril base fluids.
3. Independent parameters such as

- concentration of drilling fluids in the sediment,
- sediment oxygen consumption,
- visual appearance of sediment surface,
- deviations of pH and redox potentials,
- number of individuals of rare species and
- body size of the dominant polychaetes,

were consistent in showing biodegradation rates and environmental effects of Ultidril olefins intermediate between the two reference products Novadril II olefins and Petrofree esters.

4. A range of half-lives of 36-50 days and a mean of 43 days was found by exponential regression analyses of the decrease of concentration of olefins in the four chambers treated with Ultidril.
5. Of the two Ultidril components, the tetradecene degraded faster than the hexadecene.
6. The half-life of Ultidril olefins was intermediate between the half-life of 20 days for the Petrofree ester and 127 days for the Novadril II olefins.
7. The DF:Ba ratio as well as the oxygen consumption rates showed that biodegradation of the Novadril II olefins ceased between 62 and 100 days after deposition of the cuttings.
8. By the termination of the experiment, 0.5% of the initial concentration of Petrofree esters were present in the sediment as compared to 3-10% of the Ultidril olefins and 38% of the Novadril II olefins.

9. By combining conclusions 7 and 8 it follows that Novadril II base fluid deposits may remain present in sediments for periods of time much longer than the time predicted by the estimated half-life of 127 days.
10. Mass balance calculations indicated that 23%, 80% and 44-60%, respectively, of the initial presence of Novadril II, Petrofree and Ultidril base fluid carbon, had been completely mineralised to CO_2 during the test period. Because oxygen consumption in the chamber treated with the two latter drill fluids were still higher than the oxygen consumption in control chambers, the mineralisation fractions might continue to increase in a prolonged experiment.
11. The appearance of dead mussels and coloured patches on the sediment surface during the 27-100 days period, indicated that the treatments had affected the pore water environment in the Ultidril and Petrofree chambers more than in the control and Novadril chambers.
12. For the entire sampling period of 3-160 days, significant difference was found between the pH at 15 and 25 mm sediment depth in control chambers and the chamber treated with Petrofree esters. No other chambers showed any significant deviation of pH.
13. The redox potentials were significantly lowered at all depths (5, 15 and 25mm) in the Ultidril chambers as well as in the Petrofree chamber. The mean negative deviation for the experimental period was 75-119 mV in the Petrofree chamber and 39-48 mV for the Ultidril treatments. The corresponding negative deviation of 9-22 mV in the Novadril chamber was not significant at the 95% confidence level.
14. Analyses of the benthic fauna on day 176, showed that the total number of 155-446 individuals in each chamber were clearly dominated by the polychaete *Nereis diversicolor* and the small snails *Hydrobia ulvae & ventrosa.*
15. Compared with control chambers and chambers treated with Novadril olefins, the number of individuals was higher in the chamber treated with Petrofree esters and in three of the four chambers treated with Ultidril olefins.
16. The mean body weight of *Nereis* ranged from 10-12 mg in control sediments, via 16 mg in the Novadril chamber and 19-27 mg in the Ultidril chambers to 31 mg in the Petrofree chamber.
17. Significant correlation were found between the total sediment oxygen consumption and, respectively, total number of rare species (r=0.716) and body weight of the most dominant polychaete (r=0.919).
18. The occurrence of fewer, but larger individuals of *Nereis* in the Petrofree chamber, may have resulted from negative effects on recruitment or survival during the most intensive degradation period.
19. The macrofauna analyses revealed no clear evidence of negative effects of the moderate lowering of the redox potentials observed in the Ultidril chambers.

2. INTRODUCTION

Offshore drilling operations using oil-based mud (OBM) were prior to the late eighties a significant source of discharges of oil to the North Sea. OBMs were originally formulated on a diesel base, but environmental concern led to the development and increasing use of alternative base oils with a lower aromatic content and reduced toxicity (Dicks et al. 1986/87). After the prohibition of the discharge of cuttings containing OBM, synthetic drilling fluids have been developed and formulated into synthetic based muds (SBM). During the most recent years, the discharge of cuttings containing SBMs has increased rapidly in the Norwegian sector of 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 less than a few km from the discharge site. Elevated levels of hydrocarbons (THC) have been found out to 1-12 km from the discharge sites (Zevenboom et al. 1992). Biological effects in benthic communities may occur to 2-5 km for some installations (Reiersen et al 1989, Gray et al 1990) and perhaps beyond 10 km (Bakke et al. 1989a, Olsgaard, 1995). All of these results apply to deposition and effects of OBMs. Until now, field surveys have revealed little information about the spreading and effects of SBMs. However, effects on the benthic fauna in the vicinity of discharges of Petrofree esters have been reported at Ula and Oseberg well sites (Smith and Hobbs, 1993, Kaarstad et.al., 1994) and at well site K14-13 in the Dutch sector (Daan et al, 1995).

So far, three types of organic chemicals, namely **esters**, **ethers** and **olefins** have been introduced for mineral oil substitutes. Thus in the Petrofree mud system, the mineral oil has been replaced by a mixture of five homologous fatty acid esters, of which the main component is 2-ethylhexyl dodekanoate. Biodegradation of Petrofree esters were first investigated by Bakke and Laake, 1991, and has later been used for reference material in all tests performed by NIVA.

In the Aquamul mud system, mineral oil has been replaced by an alkyl ether with the chemical formulae $C_{20}H_{42}O_2$. Biodegradation of Aquamul ethers on cuttings have been investigated in two experiments reported by Schaanning, 1994 and Schaanning, 1995.

In the various Novadril mud systems, the mineral oil was replaced by oligomers of 1-octene (C_8H_{17}) or 1-decene ($C_{10}H_{21}$) poly-alpha-olefin compounds. Thus, cuttings containing the C_{24}-dominated Novasol I base fluid was tested by Schaanning and Laake, 1993, and cuttings containing the C_{20}-dominated Novasol II base fluid was tested by Schaanning, 1995.

The present test object was a new type of olefin base fluid, which is produced by *Schlumberger Dowell IDF* and marketed as *Ultidril.*

The objective of the present investigation was to assess the environmental fate of the the Ultidril olefin after its` deposition on the seabed as compared to the fate of Petrofree ester and Novasol II olefin base fluids on cuttings.

3. MATERIAL AND METHODS

3.1 TEST SET-UP AND ENVIRONMENTAL CONDITIONS

The test principle has been developed through several similar projects (ref. NIVA reports). The idea is to establish a series of replicate experimental systems (Figure 1), which are maintained in easily accessible indoor basins (Figure 2). Each system is referred to as a benthic chamber and the sediment environment inside the chambers is

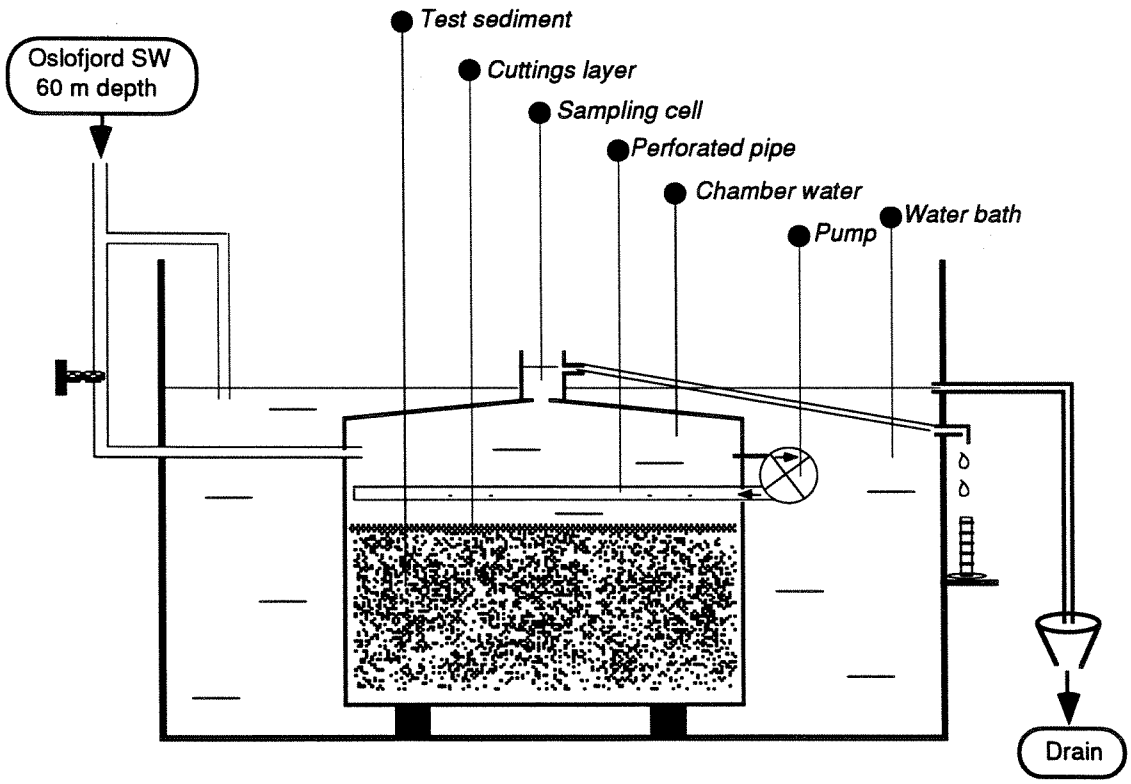


Figure 1. Schematic drawing of benthic chamber used for experimental study on biodegradation of pseudo oils on cuttings. Each chamber has a surface area of 50x50cm and a depth of 35 cm. As shown in figure 2, eight chambers were submersed in overflow water running through two large water bath trays.

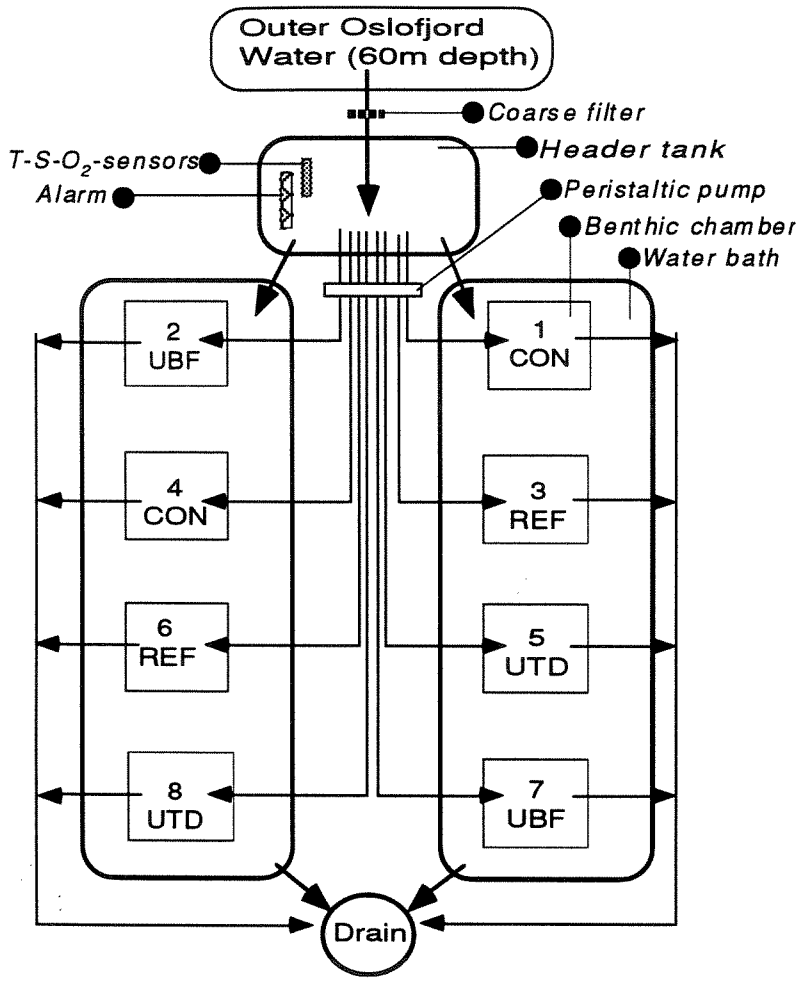


Figure 2. Schematic drawing of test set-up and water flow through the test basin.

made to simulate the conditions at the North Sea seabed as closely as suitable to the purpose.

The chambers had an area of 48 x 48 cm and a height of 35 cm. During test preparation, each chamber was filled with a bottom layer of 15 cm non-contaminated sediments left over from previous experimental work at the research station. The bottom layer was covered with a top layer of 10 cm sediment which had been recently sampled from an intertidal flat in Elingårdkilen in the Outer Oslofjord. The batch sample for the top layer was homogenised in a concrete mixer before distribution of aliquots into each chamber. Thus the top layer contained replicate macrofauna assemblages with a species composition corresponding to those surviving the procedures of transplantation from the natural habitat.

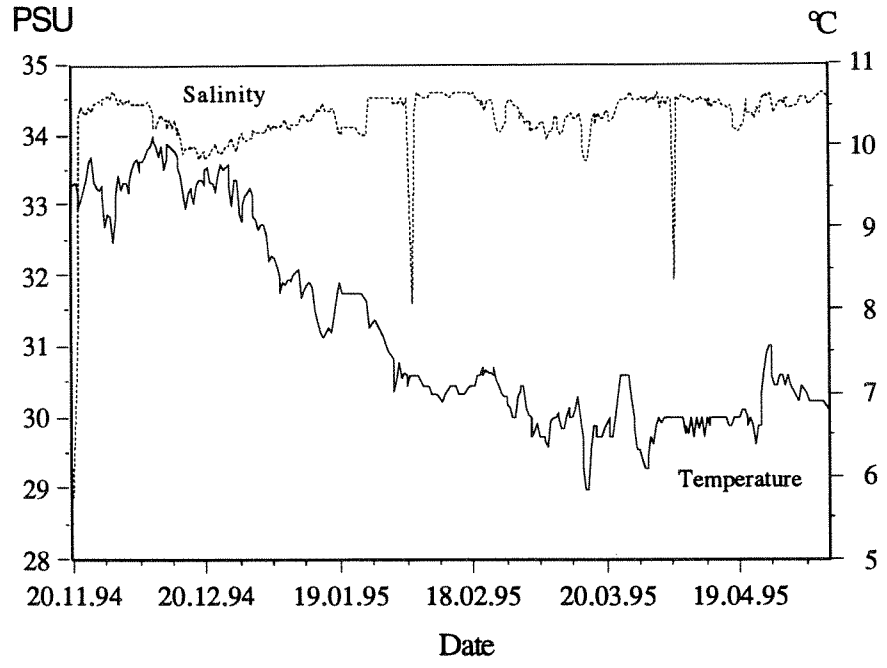


Figure 3. Temperature and salinity in header tank during experimental period.

At time zero, drill cuttings suspended in sea water were added to the overlying water in each chamber and allowed to settle on top of the test sediments. Then, chambers were covered with lids and the peristaltic pump (Figure 2) was initiated to maintain separate flows of seawater through each chamber. Thus, throughout the experimental period, the overlying water was continuously renewed with water from 60 m depth at turnovertimes of 12-32 hours.

As illustrated in Figure 1, a laminar type internal circulation system was maintained by submersed, aquarium pumps driving water through a perforated pipe positioned along one side of the chamber. By timer-control, the pumps were activated for 15 minutes every two hours. The pumps generated characteristic current velocities of 5-10 $cm \cdot sec^{-1}$. No visible resuspension of cuttings or sediments were ever observed to result from the internal circulation system.

Test conditions are summarised in Table 1. Temperature, salinity and oxygen concentration was measured daily by the Solbergstrand Environmental Monitoring Programme. As shown in Figure 3, the salinity of the source water was 33.5-34.5 PSU throughout most of the experimental period. During January, the temperature decreased slowly from a level of 9-10°C in November-December (day 0 - day 45) to a level of

Table 1. Test conditions in sediments and overlying water.

Parameter	Status
Sediment type	Marine clay, low organic content
Sediment redox state	Oxygen present at interface
Oxygen saturation	50-100% in overlying water
Temperature	Natural variations; 6-10°C
Salinity	Natural variations; 33.5-34.5 PSU
Current velocities	<1 cm.s-1 up to 10 cm.s-1
Current generation	15 min. every two hours
Illumination	Dim to dark, bright light only during sampling and inspection

about 7°C in February-May (day 75 - day 175). Temperatures in the benthic chambers were kept within ±0,5°C of the source water. By flow adjustments determined by the respiratory rates in each chamber, oxygen concentrations were maintained at concentrations 10-50% lower than the concentration in the source water.

3.2 ADDITION OF CUTTINGS

Cuttings samples and base fluids were supplied from various operators. Thus, Ultidril cuttings (UTD) as well as a small sample of unused Ultidril base fluid (UBF) were supplied from the Frøy platform, well 25/5-A5(P4), and arrived at NIVA in October 1994. Petrofree cuttings (PTF) were sampled at Treasure prospect, well 33/9-L-3H. Novadril II cuttings (PAO) were sampled from Saga's well 34/7-I-IH. Both Petrofree and Novadril samples arrived at NIVA in February 1994 and has been used in the test preceding the present. After delivery at NIVA, the cuttings samples were stored in sealed containers in the dark at 4°C. No evidence has yet been found that any degradation takes place during such storage of cuttings samples.

The cuttings were added to each chamber by making up slurries from 100 g of the respective cuttings sample, 200 g wet control sediment and a small volume of seawater. The slurry was then sprinkled into the overlying water in each chamber and allowed to settle for 20 hours. The treatment of each chamber is shown in Table 2.

In order to assess the possible impact from cuttings and mud components other than the base fluids, 82.2 g of the Ultidril Base Fluid was grinded with 263 g of dried control sediment. This mixture was aged for two days before making up the slurry for the UBF-chambers, using 40 g of this pseudo-cuttings and 260 g of control sediment.

The last two chambers (CON 1 and CON 4), were used for control purposes and treated with 300 g of wet control sediment, only. Thus, similar particle loads were added to all chambers. On the following day, the particles appeared distributed on the sediment surface of each chamber in even layers with a thickness of about one millimetre on top of the sediment.

As shown in Table 7, the doses applied during the present test corresponded to the lower range of concentrations applied in previous tests. The concentration level also correspond to levels of mineral oil (THC) frequently found up to 500 m from off-shore installations.

3.3 SAMPLING AND ANALYTICAL METHODS

3.3.1 Sediment samples

The slurries were added to the chambers 15.11.95. One sediment sample for analyses of base fluid and barium was taken from each chamber 3, 27, 62, 100, 160 and 176 days after addition. Thus, the final sampling was performed 11.05.95.

Each sediment sample was pooled from the top 0-3 cm section cut off from five separate cores (ID≈15 mm). Each core was drawn from the grid locations shown in Figure 4. The grid co-ordinates were randomly chosen using the random number function of a spreadsheet program.

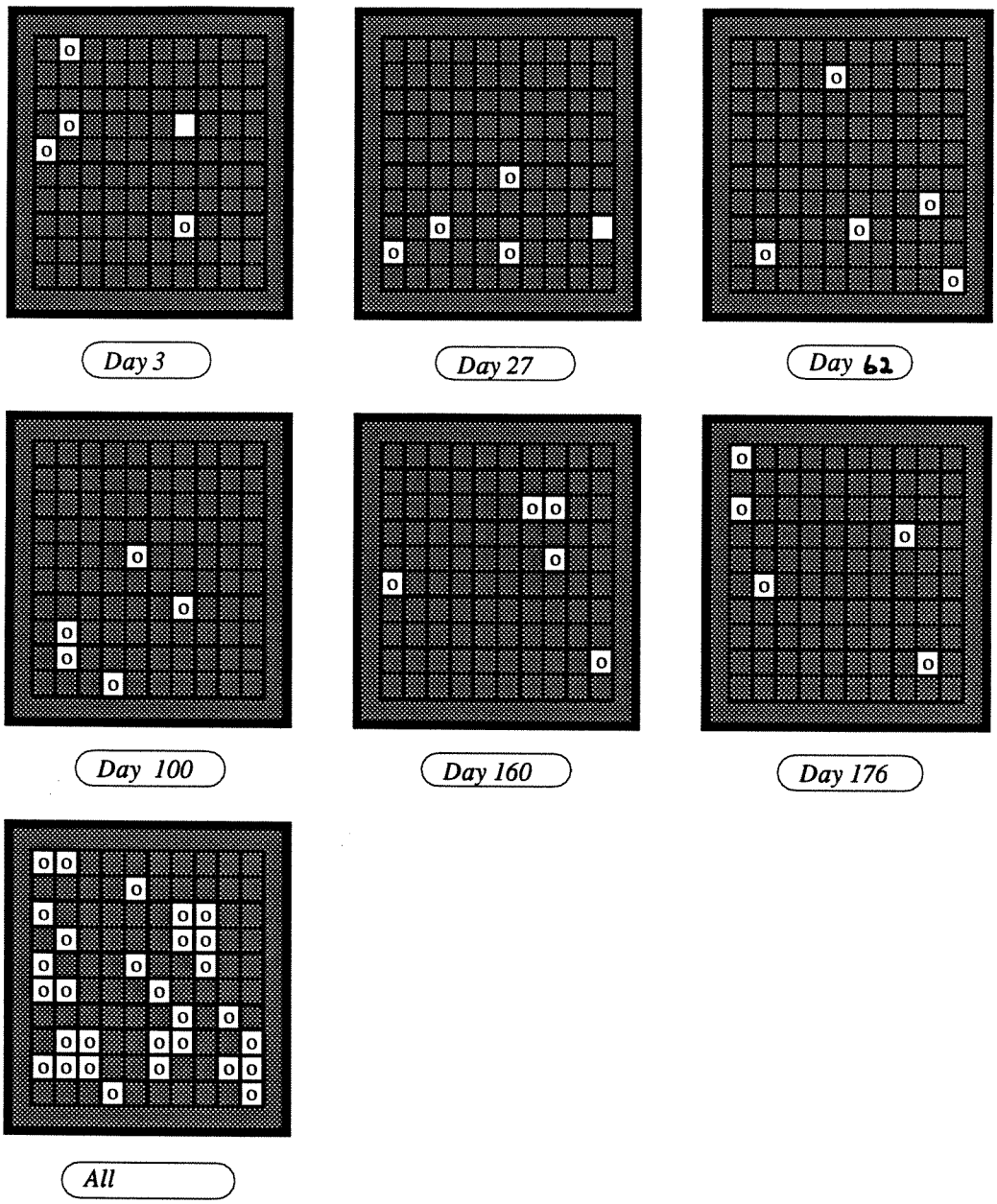


Figure 4. Grid system and randomly chosen locations for each one of the five core samples at each sampling occasion. The lower plate shows all sampled grids by the end of the experiment.

The total weight and the water content of the pooled sample was determined before the samples were put to storage at -20°C. Chemical analyses of the samples collected on day 3, 27 and 62 were performed in one batch in January and the samples collected during the remaining three surveys were analysed in a second batch in May/June.1995.

Analytical procedures are 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 a gas chromatograph using flame ionisation detector and quantitated by addition of known amounts of internal standards to each sample prior to extraction.

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

3.3.2 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 tracks and mounds on the sediment surface, the length of the core segments cut off may vary by 1-2 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, errors resulting from inaccurate sectioning would be eliminated, and provided that the entire layer containing the chemical is contained in the core segment, results reported will be independent on the length of the core segment.

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 according to particle size and mineral composition.

In the present experiment, the mass:volume ratio was determined in each sample by weighing sample containers before and after the sampling of the five core sections. The volume of the sample was 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 70°C. Thus, the concentrations of barium and drilling fluids given in appendix I table 2, were recalculated according to eq.3.1:

(eq.3.1) $C_a = M_s \cdot (100-W) \cdot C_{wght} / 5 \cdot 100 \cdot A$

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 sampled area was calculated from accurate measurements of the core diameter using a sliding calliper.

3.3.3 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, Figure 2) and in the outlet water in the sampling cell on top of each chamber (Figure 1), 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.

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

(eq. 3.2) $SOC = (C_i - C_o).F.10^3 / A.32$

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 was similar in control and treated chambers, the difference between treated and control sediment (excess SOC or ΔSOC) should correspond to the respiratory activity produced by components in the contaminants added.

3.3.4 Electrode measurements

pH and redox potentials (E_h) were determined on day 3, 27, 63, 104 and 160 after addition of cuttings. Electrodes were inserted directly into the submersed sediments at three different locations within each chamber. At each location, potentials were recorded in chamber water (OW) and 5, 15 and 25 mm below the sediment-water interface. The readings were taken as soon as the pH showed a stable value.

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 an Ag|AgCl reference electrode.

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. Thus, accurate deviations from the pH in the control sediments was emphasised more than accurate absolute values of pH in the seawater. Before each series of measurements, the pH was calibrated in standard buffers of pH 4.0 and 7.0. All calibrations and measurements were done at the experimental 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. At experimental temperature the E_h recorded in the buffer solution never exceeded a range of 437-442 mV. At 10°C the half-cell potential of the Ag|AgCl reference electrode was 231 mV (Radiometer, technical information). As recommended by ZoBell, 1946, electrode performance was checked, but not calibrated with the redox buffer. Therefore, the E_h of the samples were obtained by adding 231 mV, to the potential recorded on the Pt-electrode.

3.3.5 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.

4. RESULTS AND DISCUSSION

4.1 DRILLING FLUIDS AND BARIUM

4.1.1 Recovery of the cuttings added

300g (wet wght.) non-contaminated marine clay sediment with a low content of organic matter was added to each of the control chambers Table 2. The other chambers were treated with 200g of the same sample of "clean" sediment and 100g of the respective cuttings samples. UBF-chambers were treated with 260 g clean sediment and 40 g dried "clean" sediment soaked with 82.2 g Ultidril base fluid. Thus, all chambers received

Table 2. Initial treatment of experimental chambers and recovery of drilling fluids (DF) and barium (Ba) on the sediment surface on day 3. (na = not analysed)

	ADDED							RECOVERED		
	In suspension				Estimated on sediment			Obs. day 3/estimated		
	Sed. (g)	Cut (g)	Ba (kg^{-1})	DF (kg^{-1})	Ba ($mg \cdot cm^{-2}$)	DF ($mg \cdot cm^{-2}$)	DF:Ba ratio	DF (%)	Ba (%)	DF:Ba [1] ratio
CON 1	300	0	0.85	na	0	<0.01	-	na	na	-
CON 4	300	0	"	"	"	"	-	-	-	-
PAO 6	200	100	41.0	56.3	1.82	2.50	1.37	68.9	94.6	1.00
PTF 3	200	100	51.0	60.5	2.26	2.68	1.19	90.8	80.4	1.34
UTD 5	200	100	82.0	97.0	3.63	4.30	1.18	58.3	70.0	0.99
UTD 8	200	100	"	"	"	"	"	79.3	97.1	0.97
UBF 2	260	40	1.09	263	0.02	4.69	247	71.2	-	-
UBF 7	260	40	"	"	"	"	"	57.1	-	-

[1] Corrected for Barium background concentration of 850 $mg \cdot kg^{-1}$ dry sediment.

Table 3. Concentrations of drilling fluids observed in each chamber during the test period. Units = mg·cm^{-2}.

Day	PTF 3	PAO 6	UTD 5	UTD 8	UBF 2	UBF 7
3	2.436	1.718	2.504	3.403	3.339	2.678
27	2.336	1.426	1.993	1.547	2.559	2.275
62	1.491	1.136	1.110	1.672	2.379	1.141
100	0.211	0.818	0.964	0.852	1.510	0.898
160	0.008	0.702	0.481	0.174	0.242	0.199
176	0.011	0.660	0.150	0.097	0.340	0.114

Table 4. Concentrations of barium observed in each chamber during the test period. Units = mg·cm^{-2}.

Day	PTF 3	PAO 6	UTD 5	UTD 8	UBF 2	UBF 7
3	4.399	4.280	5.279	6.132	2.613	2.503
27	5.062	4.389	5.368	5.431	2.913	2.784
62	5.314	4.531	5.252	5.520	2.856	2.820
100	5.322	4.648	5.606	5.188	2.903	2.901
160	4.589	4.911	6.122	4.747	2.925	2.874
176	4.945	4.029	4.854	3.984	2.895	2.795

similar particle loads of 130 mg·cm^{-2} which corresponded to a nominal layer thickness of approximately 1 mm.

As calculated from GC-analyses of cuttings samples this layer should contain 2.50-4.69 mgDF·cm^{-2}. Control sediments did not contain any drilling fluids. Thus the entire amount of 1.72-3.40 mgDF·cm^{-2} observed on day 3 (
Table 3) had been added with the cuttings on day 0. As shown in Table 2, 57.1-90.8% of the added fluids were recovered in the sediment samples collected on day 3.

The cuttings prepared from control sediment soaked with base fluid contained no mud components and should not contain any barium in excess of background concentrations.

Table 5. Drill fluid:excess barium concentration ratio in chambers treated with cuttings sampled off-shore.

Day	PTF 3	PAO 6	UTD 5	UTD 8
3	1.338	1.000	0.991	0.965
27	1.056	0.952	0.810	0.612
62	0.621	0.686	0.492	0.613
100	0.088	0.463	0.348	0.367
160	0.006	0.475	0.156	0.097
176	0.005	0.541	0.072	0.079

X-ray-analyses showed a concentration of 1.09 $gBa \cdot kg^{-1}$ in the cuttings sample prepared in the laboratory. In a previous investigation, control sediments were found to contain 0.80-0.81 $gBa \cdot kg^{-1}$ dry sediment. In the present experiment, samples of the 0-3 cm layer of the UBF-chambers contained a range of 2.5-2.9 $mgBa \cdot cm^{-2}$ (Table 4), which corresponded to concentrations of 0.82-0.90 $gBa \cdot kg^{-1}$ dry sediment. Thus, the barium determined in the material added to the UBF-chambers was in reasonably good agreement with back-ground concentrations determined in control sediments. Before calculation of the DF:Ba ratios shown in Table 2 (right-hand column) and Table 4, a back-ground concentration corresponding to 0.85 $gBa \cdot kg^{-1}$ was subtracted from the concentrations observed in the chambers treated with cuttings.

The mean DF:Ba ratio of 1.23 and standard variation of 0.10 in the added cuttings samples, was not significantly different from the corresponding ratio of 1.07 ± 0.17 in the sediment samples recovered on day 3 (Table 2). In each separate chamber, the recovery of barium was frequently better than the recovery of drilling fluids. This, might result from leakage of drilling fluids during preparation and addition of the cuttings suspensions. However, the sources of errors involved in these calculations are to large to conclude any separate behaviour of the cuttings components during set-up of the experiment.

Thus, the recoveries in the sediment on day 3 of 70.0-97.1% of the barium and 57.1-90.8% of the drilling fluids added represent an improvement relative to previous tests. The results shown in Table 2 indicated a moderate loss of material during addition. The major loss of material probably resulted from suspended or poorly consolidated particles washed out of the chambers when water-flow and circulation pumps were

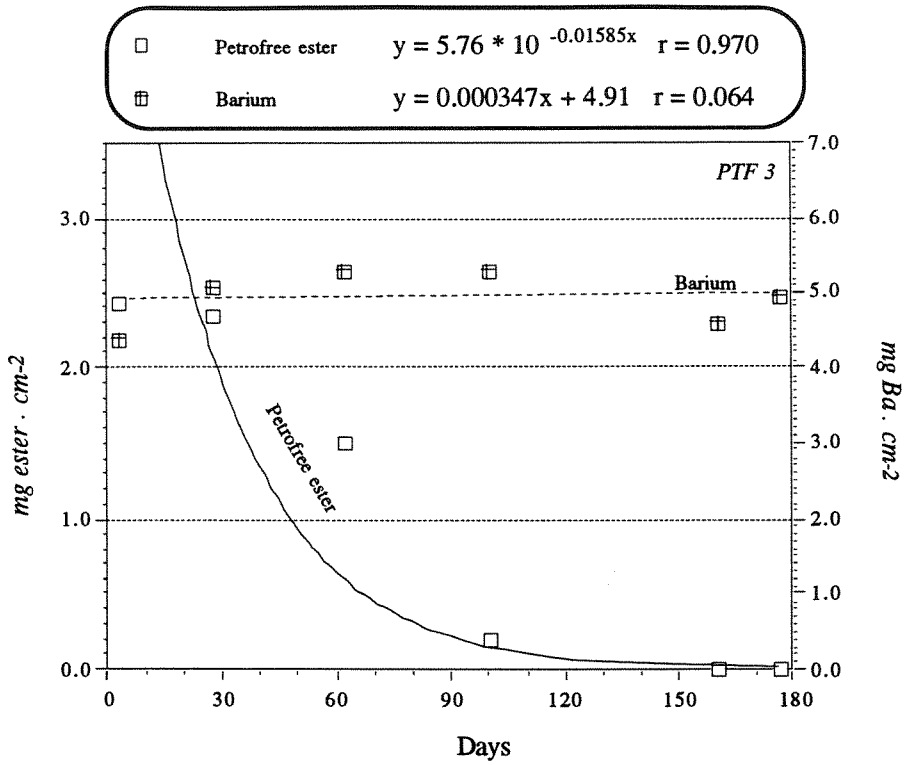


Figure 5. Variation with time of Petrofree ester and barium in 0-3 cm depth interval of sediment in chamber 3. Linear and exponential regression analyses of barium and ester, respectively, gave curves, curve equations and regression coefficients as shown.

initiated. Leakage may have contributed with a small loss of drilling fluids in some of the treatments. More than anything, however, the quite reasonable recoveries found in Table 2 confirmed the accuracy of sampling techniques, analytical methods and various assumptions implied in test set-up.

4.1.2 Loss during the test period

Results of the chemical analyses of drilling fluids and barium in the sediments are given in
Table 3 to Table 5 and in Figure 5 to Figure 8.

Barium may be considered a conservative property of the cuttings. After deposition, concentrations of barium should only change as a result of loss of cuttings particles by

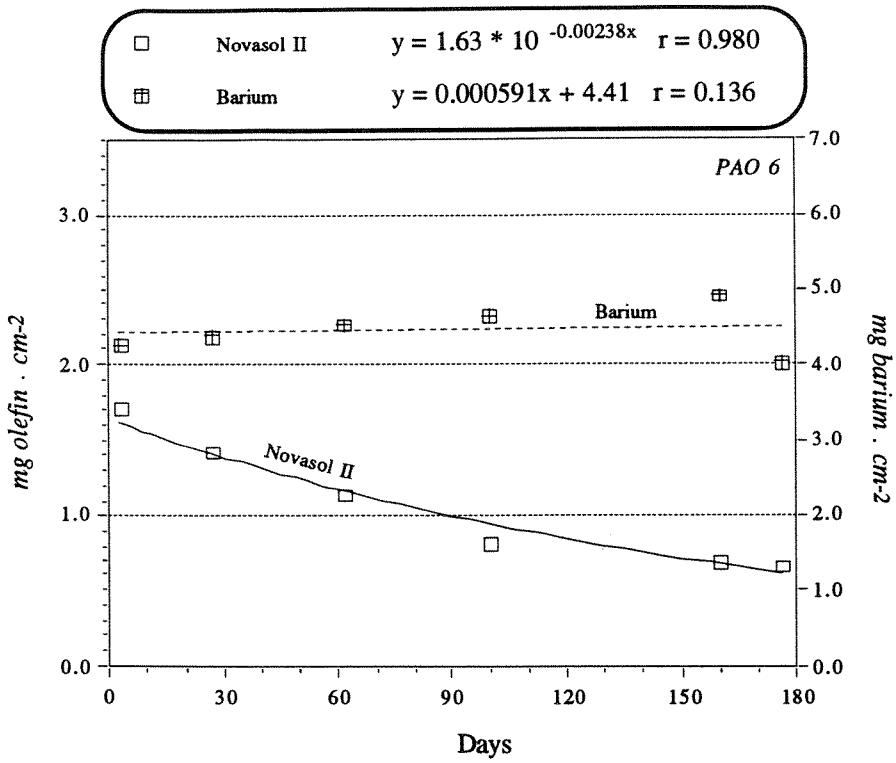


Figure 6. Variation with time of Novasol II olefins and barium in 0-3 cm depth interval of sediment in chamber 6. Linear and exponential regression analyses of barium and olefins respectively, gave curves, curve equations and regression coefficients as shown.

sampling, by resuspension to the water flowing through the chambers or by burial to sediment layers below the sampling depth of three centimetre. Thus, if relocation of cuttings particles were significant, the change of the drilling fluid:barium ratio should be a better measure on biodegradation than the change of the concentration of drilling fluids alone. Also the DF:Ba ratio will eliminate artefacts of non-representative sampling of the cuttings layer.

As shown in Table 4, apart from the downwards trend in UTD 8, no clear loss of barium was observed in any of the chambers during the course of the experiment. On the contrary, weak positive slopes were calculated by linear regression analyses as shown in Figure 5 to Figure 8 and Table 6. The concentration of the drilling fluids (Table 3), did, on the other hand, show a clear decrease with time in all chambers.

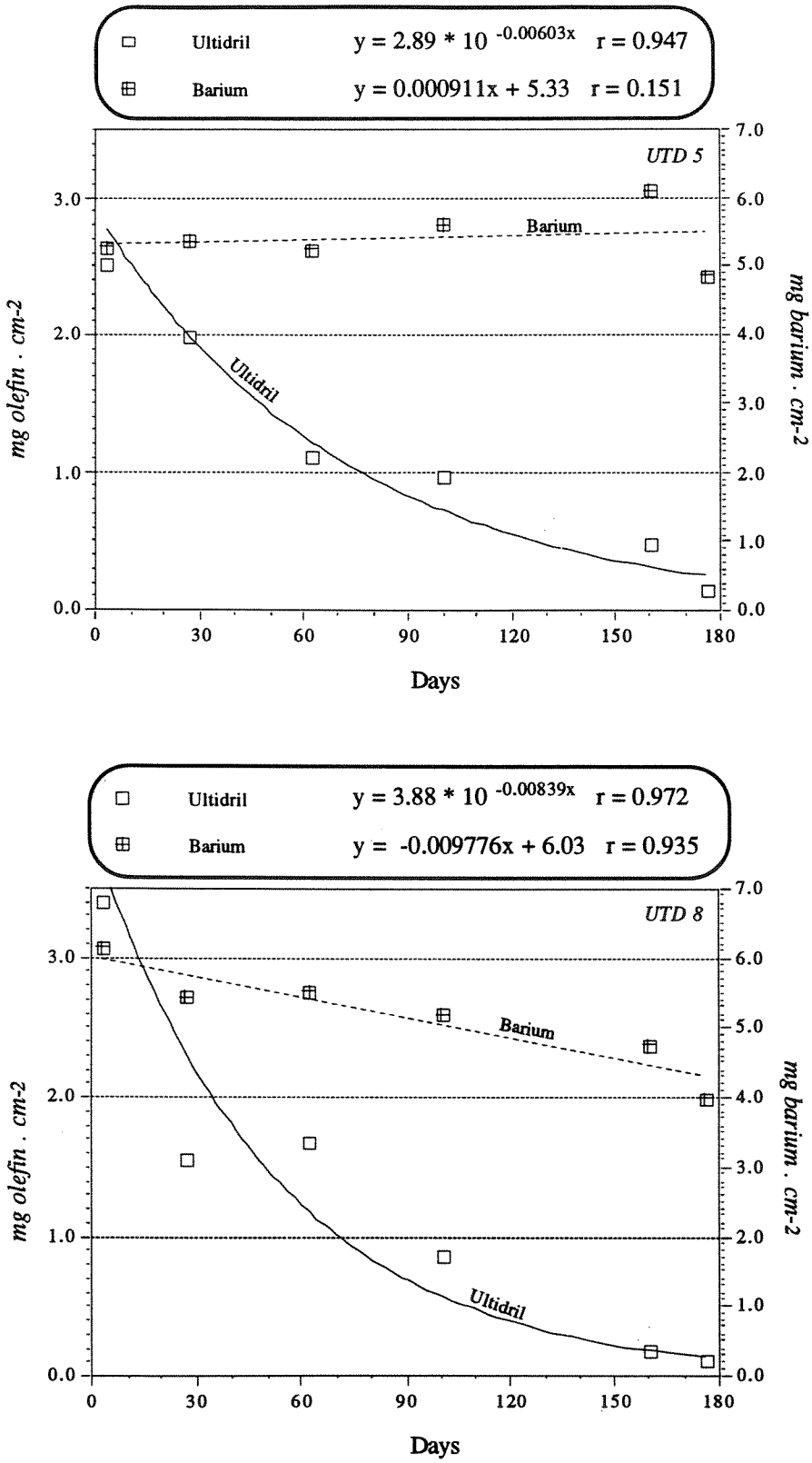


Figure 7. Variation with time of Ultidril olefins and barium in 0-3 cm depth interval of sediment in chambers 5 (upper plate) and 8 (lower plate). The two chambers were treated with cuttings sampled off-shore. Linear and exponential regression analyses of barium and olefins, respectively, gave curves, curve equations and regression coefficients as shown.

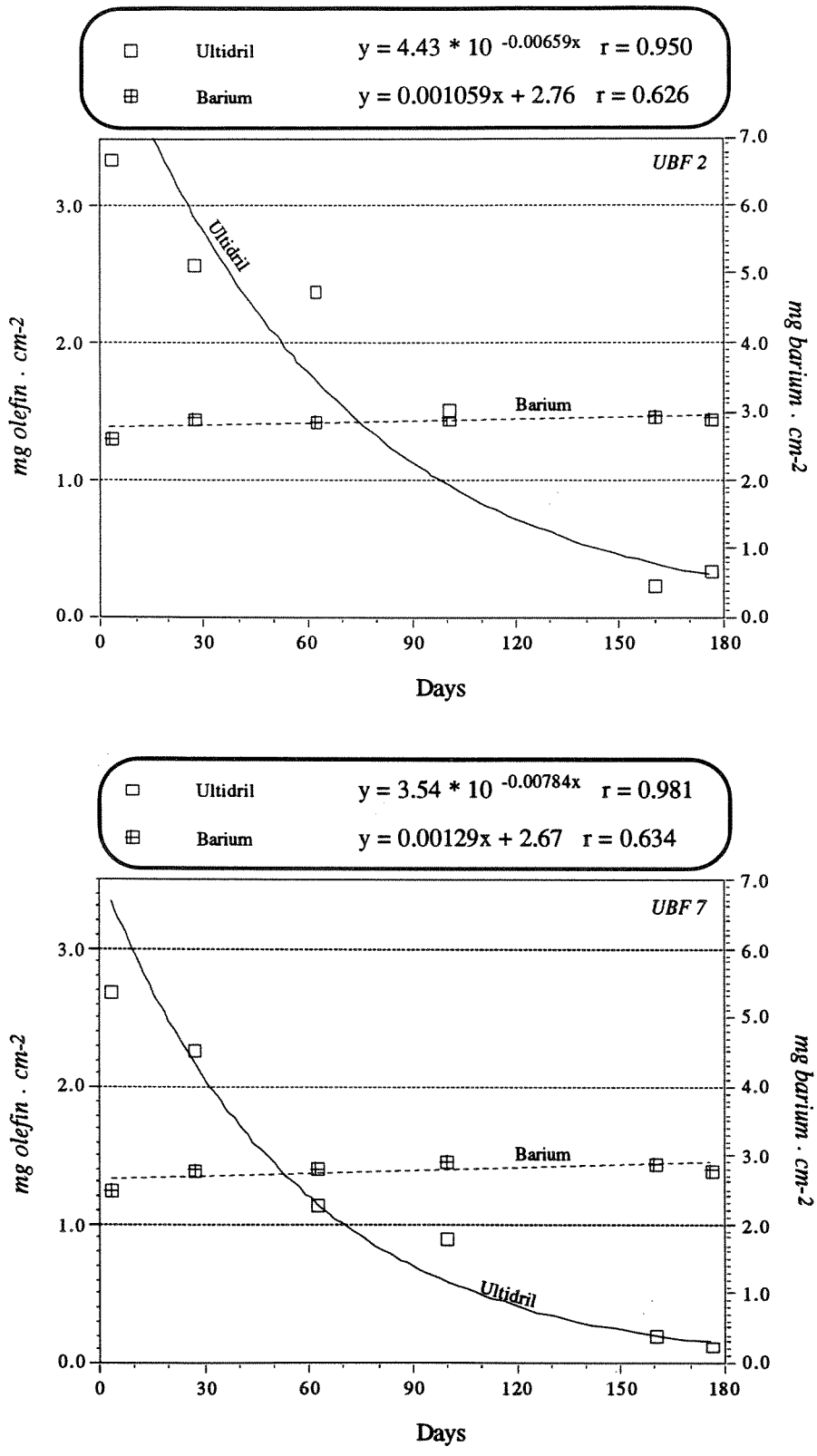


Figure 8. Variation with time of Ultidril olefins and barium in 0-3 cm depth interval of sediment in chambers 2 (upper plate) and 7 (lower plate). The two chambers were treated with control sediment soaked with Ultidril base fluid. Linear and exponential regression analyses of barium and olefins respectively, gave curves, curve equations and regression coefficients as shown.

After day 100, the concentration of Novadril olefins decreased rather slowly and the DF:Ba ratios given in Table 5, showed no decrease at all. Thus the slow loss of Novadril base fluids observed during the last 76 days (
Table 3), may be fully accounted for by a slow loss of cuttings particles or, simply, by artefacts of non-representative sampling of the cuttings layer.

Apart from the observation in UBF 2 on day 176, the concentration of Ultidril olefins declined throughout the experiment, absolute (
Table 3) as well as relative to concentrations of barium (Table 4).

In previous studies, first order kinetics have been found more or less appropriate for the description of the loss of drilling fluids with time. The general form of a first order reaction is:

(eq.4.1) $C = C_0.10^{-kt}$

in which:

C = concentration at time t
C_0 = initial concentration

t = time
k = rate constant

From eq. 4.1 it can be shown that if the half-life τ is the time at which $C = C_0/2$, $\tau = 0.302/k$.

The curve fits plotted in Figure 5 to Figure 8 show the best fit of observations of drilling fluids to exponential models of the general form given in eq.4.1. Correlation coefficients (r) and half-lives (τ) calculated from regression constant (k) are given in Table 6. The barium data were fitted to linear regression models.

The significance of each trend is given by the correlation coefficient r. For six observations and four degrees of freedom, the critical value of r is 0.87 at the 95% confidence level (Pearson and Hartley, 1966). Thus, the range of correlation coefficients for the drilling fluids of 0.94 - 0.98 (Table 6) showed significant decrease during the test period of all drilling fluids in all chambers. Significant loss of barium was only observed in UTD 8. The other chambers gave weak positive trends, but those were not significant.

Table 6. Regression constants (k, slope), half-lives (τ) and correlation coefficients (r) calculated by regression analyses of drilling fluids and barium in each chamber. All data, curves and curve equations are shown in Figure 5 to Figure 8. The yes/no means significant/not significant change of concentration at 99% confidence level.

Cham-ber	Base fluid (exponential regression) k	τ (days)	r	sig-nificant?	Barium (linear regression) slope		sig-nificant?
UTD 5	-.00603	49.9	.947	yes	.00091	.151	no
UTD 8	-.00839	36.0	.971	yes	-.00978	.935	yes
UBF 2	-.00659	45.8	.950	yes	.00106	.626	no
UBF 7	-.00784	38.5	.981	yes	.00129	.634	no
PTF 3	-.01585	19.6	.970	yes	.00059	.136	no
PAO 6	-.00238	127	.980	yes	.00035	.064	no

Table 7. Summary of initial concentrations, half-lives and oxygen consumption data obtained in benthic chambers during the period 1992-95.

	Init. conc. $mg \cdot cm^{-2}$	Half-life days	Mean SOC $\mu mol \cdot m^{-2} \cdot h^{-1}$	Max SOC	Reference
Control			220	590	*Test 1993*
Control			170	330	*Test 1994*
Control			220	390	*This test*
Mineral oil	3.2	399	550	880	*Test 1993*
Mineral oil	3.2-5.3	199			*Review of half-lives, 1995*
Aquamul	13.9	464	550	840	*Test 1993*
Aquamul	15.1	158	490	700	*Test 1994*
Aquamul	13.3-17.9	200			*Review of half-lives, 1995*
Novadril I	3.2-15.1	368			*Review of half-lives, 1995*
Novadril II	8.1	207	480	820	*Test 1994*
Novadril II	6.3-9.9	207			*Review of half-lives, 1995*
Novadril II	1.7	127	320	710	*This test*
Petrofree	4.2	20	890	1460	*Test 1993*
Petrofree	16.5	92	1370	2270	*Test 1994*
Petrofree	3.5-17.2	31			*Review of half-lives, 1995*
Petrofree	2.4	20	760	1420	*This test*
Ultidril	3	43	610	1030	*This test*

The observed half-life of 19.6 days for the Petrofree ester confirmed results from previous tests run at similar initial concentration levels (see Table 7, and Bakke and Laake, 1991). At the 4-6 times higher initial concentrations applied in the test in 1994 (Table 7), the half-life of the Petrofree esters was found to be 92 days. If a similar dependence on initial concentration applies to the Novadril II olefins as well, the present observation of a half-life of 127 days compared reasonably well with the half-life of 207 days determined at 4-5 times higher initial concentrations in the test in 1994.

For the four chambers treated with Ultidril olefins, half-lives ranged between 36.0 and 49.9 days (Table 6). Mean half-life was 42.6 days. As shown in Table 7, apart from the short half-life of the Petrofree esters, the half-life of Ultidril olefins was shorter than the half-life of any other drilling fluid tested so far. Unfortunately, the Aquamul ethers have only been tested at the higher range of concentrations, but in the recent review of half-lives, the half-life of Aquamul ethers was concluded not likely to be much different from the half-life of Novadril II olefins (Schaanning, 1995b).

4.1.3 Chemical structure and relative degradability of Ultidril components

The results of the GC/MS analyses (Appendix III) showed that the Ultidril base fluid was composed of a mixture of two unsaturated olefin compounds with the chemical formulae $C_{14}H_{28}$ and $C_{16}H_{32}$.

The two components appeared as sharp peaks in the gas chromatograms. The area below each of the two peaks was calculated separately. Thus any change with time of the C_{14}: C_{16} sum area ratio should reveal any difference with regard to the degradability of the two components. As shown in table 3.3 in Appendix III, the C_{14}: C_{16} ratio decreased throughout the experimental period from 1.8 on day 3 to 0.61 on day 176. This showed that the C_{14} component degraded faster than the C_{16} component.

4.2 OXYGEN CONSUMPTION

Oxygen consumption in the chambers was calculated from bi-weekly observations of flow rate and decline of oxygen concentration between in- and out-let from each chamber as described in section 3.3.3.

As shown in Table 8, the mean oxygen concentration was 7.8 $mg \cdot kg^{-1}$ at the inlet and 5.3-6.9 $mg \cdot kg^{-1}$ at the various outlets. If oxygen dropped to values below 4.0 the flow rate through the chamber was immediately increased. Thus, the lowest oxygen concentrations shown in Table 8 were never allowed to prevail for more than 2-3 days.

Table 8. Mean values and variations during the experimental period of temperatures in the header tank and concentration of oxygen and flow rates through each chamber.

	Mean	Max.	Min.	Std. dev.	n	Missing
Temperature (°C)						
Header tank	7.8	10.2	6.3	1.3	48	0
Oxygen ($mg \cdot kg^{-1}$)						
Header tank	7.8	9.5	6.4	0.8	46	2
1-CON	6.3	7.7	4.7	0.8	46	2
4-CON	6.3	7.5	5.0	0.7	45	3
5-UTD	6.2	7.6	5.0	0.7	46	2
8-UTD	6.1	7.8	4.7	0.8	46	2
2-UBF	5.9	7.3	3.1	0.7	46	2
7-UBF	5.9	7.1	4.7	0.6	46	2
6-PAO	6.9	8.8	5.5	0.8	46	2
3-PTF	5.3	6.7	3.6	0.9	46	2
Flow ($ml \cdot min^{-1}$)						
1-CON	19	38	12	5.4	48	0
4-CON	18	27	13	3.6	48	0
5-UTD	47	63	31	9.9	48	0
8-UTD	41	51	27	6.8	48	0
2-UBF	39	52	24	8.7	48	0
7-UBF	40	59	24	9.6	48	0
6-PAO	42	61	17	10.4	46	2
3-PTF	36	55	17	9.9	48	0

Table 9. Excess cumulative oxygen consumption ($mmolO_2 \cdot m^{-2}$) at various points of time during the experimental period.

Day	PAO 6	PTF 3	UTD 5	UTD 8	UBF 2	UBF 7
30	191	462	339	333	236	322
61	323	1143	650	667	528	684
90	425	1541	982	994	907	1036
121	456	1873	1274	1277	1181	1342
147	451	2105	1464	1458	1378	1534
174	427	2267	1617	1602	1571	1720

This test strategy implied that in order to maintain similar concentrations of oxygen, some variation of flow rates between the chambers had to be accepted. If the higher flow rates had implied higher current velocities at the sediment water interface, increased oxygen supply to sediment organisms and a higher sediment oxygen consumption might have occurred. However, the highest flow rates shown in Table 8, correspond to no more than rapid dripping from the outlet tubes. The water movements imposed by these flow rates were small compared to the movements generated by the circulation pumps. Thus, the dominating impact of the circulation pumps (section 3.1), ensured very similar current regimes in each chamber.

Results of the sediment oxygen consumption measurements are shown in Table 9, Figure 9 and Figure 10. Figure 9 shows the variation of instantaneous rates of the consumption of oxygen in treated chambers in excess of the oxygen consumption in control chambers. Thus, Figure 9 was assumed to describe the oxygen consumed by added contaminants, only. Figure 10 shows the development of the total accumulated oxygen consumption in all chambers.

In the Petrofree chamber, oxygen consumption increased rapidly after addition and reached maximum rates just above 1400 $\mu molO_2 \cdot m^{-2} \cdot h^{-1}$ at about day 50. Then consumption rates declined rapidly and, as shown in Figure 9, from day 70 until the termination of the experiment, oxygen consumption in the Petrofree chamber was not much different from the oxygen consumption in the four Ultidril chambers. A more or less linear decline from 600-720 $\mu molO_2 \cdot m^{-2} \cdot h^{-1}$ on day 69 to 380-520 $\mu molO_2 \cdot m^{-2} \cdot h^{-1}$ on day 174 was observed in the Ultidril and Petrofree chambers. In the two control chambers, the rates varied moderately (one standard deviation = 70 $\mu molO_2 \cdot m^{-2} \cdot h^{-1}$)

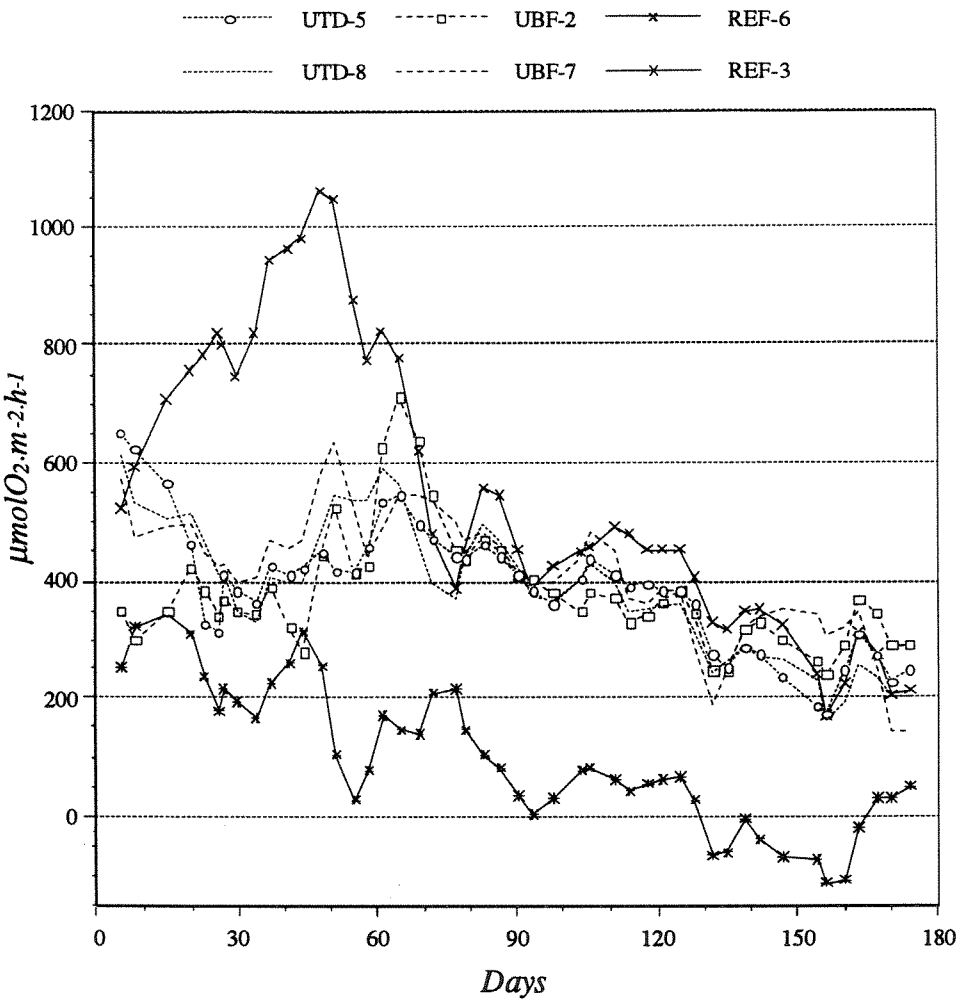


Figure 9. Rates of oxygen consumption in chambers treated with cuttings and base fluids in excess of the oxygen consumption measured in control chambers treated with clean sediment. Data were smoothed using a 3 point binomial function. REF 6 = PAO 6 and REF 3 = PTF 3.

about a mean of 220 $\mu molO_2 \cdot m^{-2} \cdot h^{-1}$. Thus, by the time of the final sampling, the rate of oxygen consumption in the Petrofree chamber as well as in the four chambers treated with Ultidril, were still more than twice as high as the rates observed in the control chambers.

It appears from Figure 9 that in the Novadril chamber, a decline of oxygen consumption rates occurred from a level about 250 $\mu molO_2 \cdot m^{-2} \cdot h^{-1}$ during the initial 0-50 days period to rates not much different from control chambers during the last 90-176 days period. As shown in Table 9, in this chamber, the excess cumulative oxygen consumption

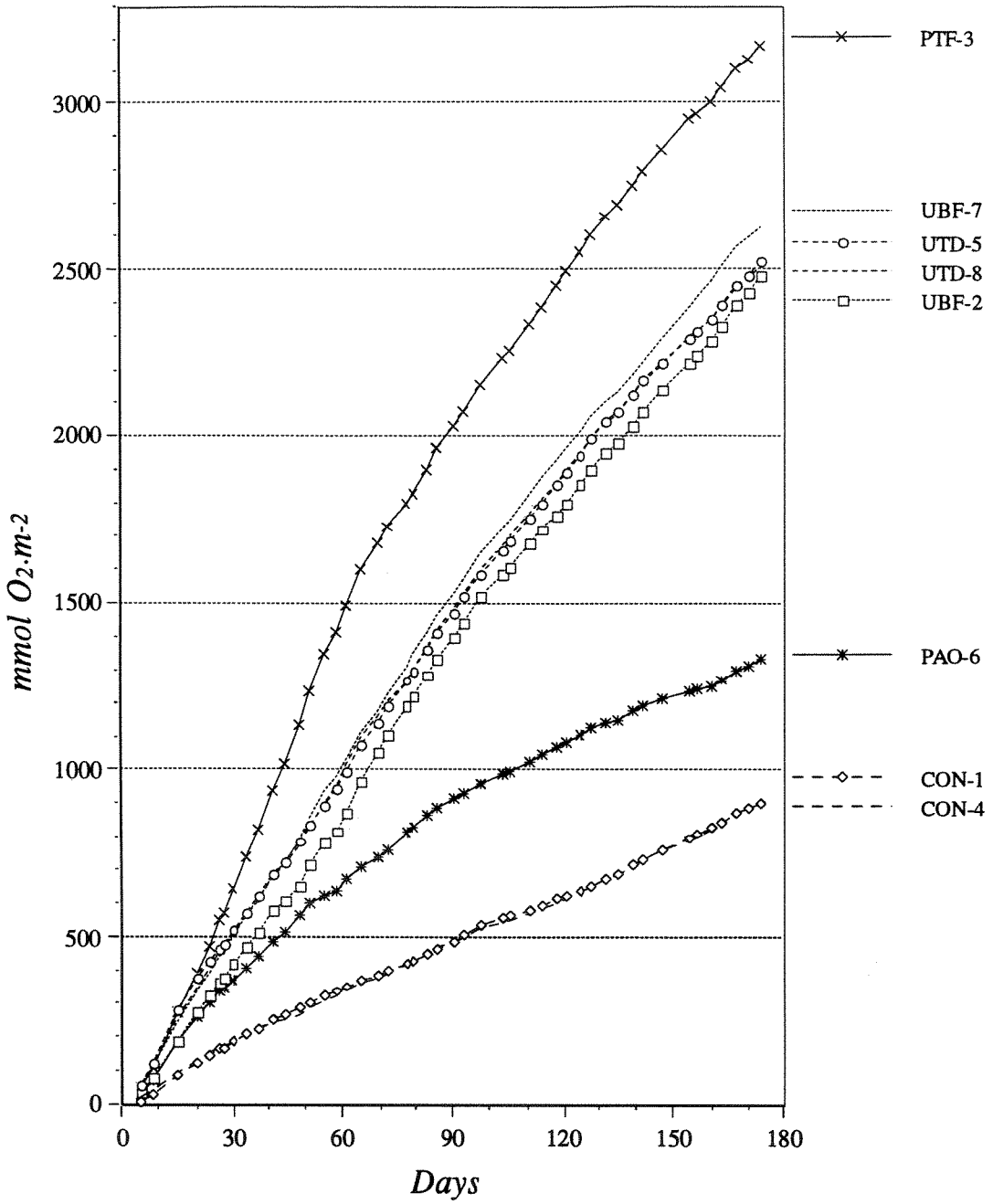


Figure 10. Cumulative sediment oxygen consumption in each chamber during the 176 days experimental period.

culminated on day 128, and no net uptake of oxygen was observed after day 90. The absence of any net respiration during the 90-174 days period was consistent with the-negligible loss of olefins and the constant olefin:Ba ratio observed in the sediment samples collected during the 100-176 days period (
Table 3 and Table 5).

The observed trend of oxygen consumption in the Petrofree chamber, was characterised by very high consumption rates culminating 1-3 months after deposition of the cuttings. Similar trends have been observed in preceding tests. The actual maximum rates and extension of the period of intensive degradation depend on initial concentration of esters. Thus, with regard to half-life and oxygen consumption in the Petrofree treatments, the test in 1993 (Table 7) compared very well with the present test.

In the test in 1994, chambers treated with initial concentrations of 6.3-9.9 $mg \cdot cm^{-2}$ Novadril II olefins yielded maximum excess oxygen consumption rates of 300-400 $\mu mol O_2 \cdot m^{-2} \cdot h^{-1}$. Similar maximum rates were observed in the present test (Figure 9). In the first test, however, the high level was maintained throughout the experimental period as opposed to the early decline in the present test. Thus the primary impact of higher doses of Novadril II appeared to be an extension of the degradation period.

Conclusively, taking differences in initial concentration of base fluids into consideration, the present results on oxygen consumption in chambers treated with the two reference fluids, were consistent with results obtained in previous tests (Table 7). Furthermore, comparing maximum and mean rates of sediment oxygen consumption, Novadril II olefins were in the 1994 test found to behave quite similar to Aquamul BII ethers. In the test in 1993, however, the Aquamul ethers were found to behave very similar to mineral oil. Thus, from the fact that in the present test, oxygen consumption in the Ultidril chambers was significantly higher than the oxygen consumption in the Novadril chambers (Table 7), it follows that the Ultidril olefins are not only more degradable than Novadril II, but also more degradable than Aquamul BII ethers and mineral oil.

4.3 MASS BALANCE OF DRILLING FLUIDS

In this section the mechanisms responsible for the observed loss of drilling fluids from the sediment between day 3 and day 176 shall be elucidated in a mass balance budget. Separate budgets for each chamber is shown in Table 10 in concentration units as well as normalised to the initial sediment concentration.

The primary input in the budget was the concentration of drilling fluids determined in samples of the 0-3 cm section of the sediments on day 3 and day 176. The difference between final and initial concentration was taken to represent the total loss over the period. This total loss was assumed to result partly from biodegradation of drilling fluid carbon to CO_2, and partly from loss of drilling fluids attached to cuttings particles. The deficit, which will represent an object of speculation, may result from errors and false assumptions or processes for which the data required for quantitation is absent or inadequate.

The item "respired" was calculated from the accumulated excess oxygen consumption (Table 9) and the theoretical amount of oxygen required to oxidise an average drilling fluid carbon atom to CO_2. The conversion factors derived from the information available on the stoichiometric formula of each drilling fluid, were 3.45 $mgO_2 \cdot mg\ olefin^{-1}$ and 2.97 $mg\ O_2 \cdot mg\ ester^{-1}$.

The item "barium correction" was estimated from the relative decrease of the concentration of barium given by the slopes of the regression curves shown in Figure 5 to Figure 8. A significant decrease of barium was only observed in UTD 8. Because loss of barium was only observed in one chamber, the loss was more likely to result from non-representative sampling of the cuttings layer rather than any real process removing cuttings particles from UTD 8 only. In either case, the calculated loss of 28.8% of the initial concentration should apply to drilling fluids as well as barium.

The budget (Table 10) showed that whereas complete mineralisation to CO2 could account for 80% of the loss of Petrofree esters, this process could only account for 23 % of the loss of Novadril II olefins. Mineralisation could account for 44-60% of the loss of Ultidril olefins. As argued above, the apparent loss of barium in UTD 8 may indicate an overestimation of the initial concentration of drilling fluids in this chamber. Thus, at least one of the two low normalised values of 44% respiration loss may result from

overestimated initial concentration. Furthermore, as shown in Figure 9, the oxygen consumption rates in PTF 3 as well as in all chambers treated with Ultidril was higher

Table 10. Mass balance of drilling fluids in each chamber (see text).

	PAO 6	PTF 3	UBF 2	UBF 7	UTD 5	UTD 8
Units = mg DF·cm^{-2}						
In sediment day 176	0.66	0.01	0.34	0.11	0.15	0.10
+ respired	0.40	2.44	1.46	1.60	1.50	1.49
+ barium correction	0.00	0.00	0.00	0.00	0.00	0.95
+ other loss	0.66	0.60	1.54	0.97	0.85	0.86
= in sediment day 3	1.72	3.05	3.34	2.68	2.50	3.40
Normalised						
In sediment day 176	38 %	0 %	10 %	4 %	6 %	3 %
+ respired	23 %	80 %	44 %	60 %	60 %	44 %
+ barium correction	0 %	0 %	0 %	0 %	0 %	28 %
+ other loss	39 %	20 %	46 %	36 %	34 %	25 %
= in sediment day 3	100 %	100 %	100 %	100 %	100 %	100 %

than in the control chambers by the termination of the experiment. Thus, in a prolonged experiment, mineralisation of esters and Ultidril olefins would continue to increase further towards the theoretical 100%, whereas the mineralisation of Novadril olefins appeared to have ceased at 23%. In our previous test of Novadril II olefins, respiration had not ceased when the final samples were taken and mineralisation to CO_2 could only account for 10-18% of the initial concentration.

Thus, the results of the present test indicated that a significant fraction of the Novadril II olefins may remain present in the sediments for a period of time longer than the time predicted by the half-life. No indications were found of a similar refractory fraction of Petrofree esters or Ultidril olefins.

The budget was balanced with the item called "other loss". The deficit varied between 20% and 46% and, as more fully discussed in previous reports, may be accounted for by

- leakage of drilling fluids or metabolites to overlying water,
- metabolites still present in the sediment but not detectable in the chemical analyses (not mineralised drill fluid carbon), or
- alternative degradation processes (not observed mineralisation).

4.4 EFFECTS OF ADDITION OF CUTTINGS

4.4.1 Visual effects

Visible changes on the sediment surface will often be strong evidence of the occurrence of dramatic changes in the sediment environment. For this reason, any obvious appearances on the sediment surfaces in each chamber was noted at each sampling occasion.

On day 3, when the turbidity had disappeared from the water column, the added material was present as a thin "carpet"-like layer on top of the sediments. Numerous small holes revealed the presence of an active macrofauna community perturbing the recently deposited material. Tracks in the "carpets" 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.

During sampling on day 27, the sediment surfaces in the two control chambers and PAO-6 was uniformly grey. In all four chambers treated with Ultidril, small yellow spots had appeared on the sediment surface. In PTF 3, the yellow spots were somewhat more abundant than in the Ultidril chambers and a few black spots were noted. Black spots are frequently associated with the occurrence of hydrogen sulphide in the pore water and precipitation of FeS.

On day 63, the control and PAO- chambers were still grey and the yellow patches were observed in all Ultidril chambers. In the Petrofree chamber approximately 80% of the sediment surface had turned black and white spots associated with sulphide oxidising bacteria had appeared on top of the black areas. A few empty shells of a small (≈5 mm) mussel was found on the sediment surface in all treated chambers, but none in the controls (Table 11).

On day 100, the visual appearance was essentially unchanged relative to day 63. Photographs of the open chambers (Figure 11) shows the black and yellow areas

Table 11. Counts of dead mussels on the sediment surfaces on days 62, 100 and 160.

Day	PAO 6	PTF 3	UBF 2	UBF 7	UTD 5	UTD 8	CON 1	CON 4
62	1	6	1	4	3	5	0	0
100	2	6	2	5	4	9	1	0
160	2	7	3	4	9	8	2	2

covering more than 90% of the sediment surface in PTF 3, as opposed to the light appearance of the other chambers.

On day 160, the white spots and most of the black areas had disappeared from PTF 3. The two control chambers still appeared evenly grey, whereas all the treated chambers appeared spotted grey and brown.

The estimated number of shells, given in Table 11, should not be considered an accurate measure. Nevertheless, it tend to reveal a consistent difference between control and treated chambers. If the mussels observed on the sediment surfaces had escaped from adverse conditions in the pore water, the mussel counts tend to suggest the occurrence of less tolerable conditions in the pore waters of the PTF and the Ultidril chambers, as compared to control and the Novadril chamber. This was consistent with the higher oxygen consumption rates in PTF and Ultidril chambers and indicated that even though no indications were found on the presence of hydrogen sulphide in the Ultidril sediments, sensitive species had been adversely affected.

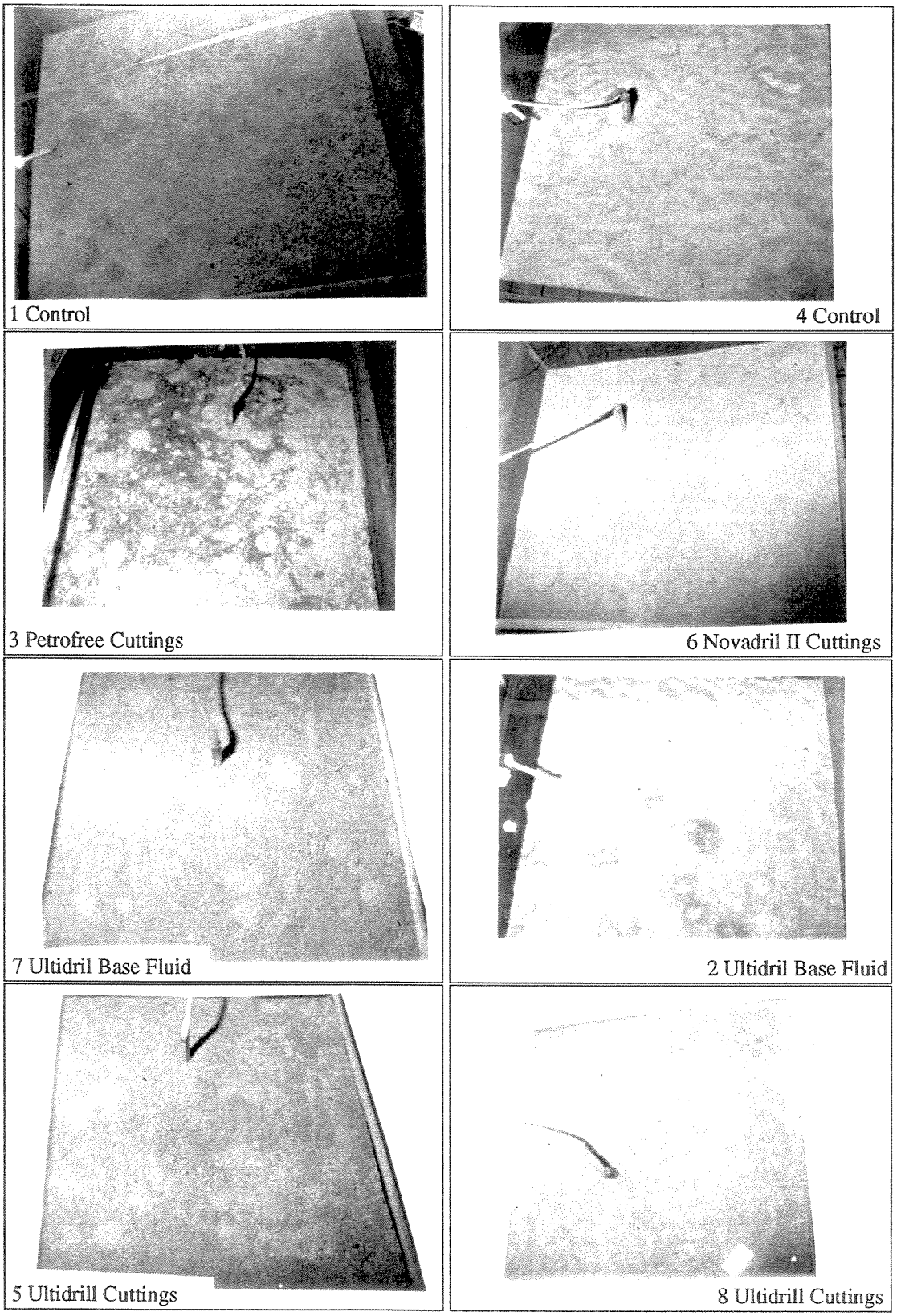


Figure 11. Photographs of sediment surface in each chamber taken 100 days after addition of cuttings.

4.4.2 pH and redox potential deviations

All measurements of pH and redox potentials are given in appendix . Table 12 shows the pH and E_h observed in control chambers at three sediment depths. Differences between the pH and redox potentials observed at each depth and time in the treated chambers and the corresponding observations in the control chambers are shown in Table 13, Table 14 and Figure 12. The tables also show probabilities calculated by ANOVA analyses using the SYSTAT© statistical software for the Macintosh (Tukey HSD multiple comparisons). Table 15 shows the corresponding statistical analyses for the entire 3-160 days sampling period.

pH variations were small and well within the normal range of pH values found in non-polluted marine sediments. In the chamber water the pH ranged 7.8-8.0. In most chambers, pH decreased with depth to values between 7.3-7.6 at 25 mm depth in the sediment.

The maximum negative deviations of pH occurred at 15-25mm depth in the Petrofree chamber on day 104 (Figure 12). Between day 104 and 160, this negative deviation was turned into a small positive deviation. The pH in the control chamber changed negligibly during the same time interval (Table 12). When sulphate reduction slows down and accumulated reduced species such as NH_4^+, H_2S, FeS, Fe^{2+}, Mn^{2+} become reoxidised, a number of basic reactions may occur to drive the pH in an upwards direction. Thus, an increase of the pH such as the one observed in the Petrofree chamber should be expected to occur towards the end of an anoxic event.

Table 12. Observations of pH and E_h in control sediments. Values are mean and standard deviations of six determinations in two separate chambers.

	pH			E_h (mV)		
Sed. depth:	5 mm	15 mm	25 mm	5 mm	15 mm	25 mm
Day 2	7.84 ± .02	7.72 .09	7.54 ± .09	320 ± 41	209 ± 37	155 ± 25
Day 27	7.83 ± .11	7.70 ± .10	7.58 ± .08	304 ± 28	217 ± 27	156 ± 31
Day 63	7.72 ± .12	7.56 ± .02	7.47 ± .04	370 ± 7	233 ± 18	183 ± 13
Day 104	7.94 ± .01	7.78 ± .10	7.64 ± .08	327 ± 29	226 ± 27	153 ± 23
Day 160	7.92 ± .04	7.61 ± .28	7.64 ± .14	270 ± 38	179 ± 10	138 ± 9

Table 13. Mean difference of pH in treated versus control sediments. Probabilities are shown in the right-hand columns and bold numbers highlight significant differences.

	ΔpH (treated-control)			probability (p)		
	5 mm	15mm	25mm	5mm	15mm	25mm
Novadril						
Day 3	-0.03	-0.13	-0.04	1.000	0.509	1.000
Day 27	0.05	0.02	0.05	0.993	1.000	1.000
Day 63	0.05	0.10	0.12	0.991	0.842	0.788
Day 104	0.01	0.00	0.03	1.000	1.000	1.000
Day 160	0.05	-0.01	-0.03	0.344	1.000	1.000
Petrofree						
Day 3	-0.10	-0.16	-0.12	0.478	0.195	0.832
Day 27	-0.01	-0.11	-0.17	1.000	0.775	0.343
Day 63	-0.02	-0.12	-0.09	1.000	0.657	0.969
Day 104	-0.06	-0.28	-0.27	0.166	**0.006**	**0.041**
Day 160	-0.02	0.08	0.04	0.998	0.974	1.000
Ultidril base fluid						
Day 3	-0.02	-0.07	-0.06	1.000	0.957	0.994
Day 27	0.05	-0.08	-0.06	0.960	0.887	0.994
Day 63	-0.01	-0.09	-0.08	1.000	0.795	0.946
Day 104	-0.02	-0.03	-0.06	0.991	1.000	0.989
Day 160	0.00	-0.05	-0.02	1.000	0.997	1.000
Ultidril cuttings						
Day 3	-0.01	0.03	0.02	1.000	1.000	1.000
Day 27	0.04	-0.09	-0.06	0.994	0.750	0.995
Day 63	0.06	-0.06	-0.15	0.883	0.981	0.192
Day 104	-0.01	-0.10	-0.04	0.998	0.696	1.000
Day 160	-0.02	-0.07	-0.09	0.983	0.948	0.924

A similar increase of the pH deviation was observed in the Novadril chamber during the initial 3-60 days sampling period. The high redox potential showed that any reservoirs of reduced forms of sulphur, iron and manganese must have been low in the Novadril chamber. Rapid increase of concentrations of ammonium have been observed in pore waters immediately after addition of organic material. However, amino nitrogen is not known to be abundant in cuttings samples. Thus, the increase of the pH-deviation in the Novadril chamber, should rather be considered a result of the combined action of small amounts of alkaline buffers added with the cuttings (many mud types contain alkaline buffers which trigger much larger pH deviations than those discussed here), and the absence of high rates of carbon oxidation which controlled the pH lowering in the chambers treated with esters and Ultidril olefins.

Table 14. Mean difference of redox potentials in treated versus control sediments. Probabilities are shown in the right-hand columns and bold numbers highlight significant differences.

	ΔE_h (treated-control)			probability (p)		
	5 mm	15mm	25mm	5mm	15mm	25mm
Novadril						
Day 3	-2	-23	-43	1.000	0.955	0.754
Day 27	-38	-56	-20	0.995	0.820	1.000
Day 63	25	7	-1	1.000	1.000	1.000
Day 104	-23	-45	-20	0.998	0.740	0.998
Day 160	-8	7	3	1.000	1.000	1.000
Petrofree						
Day 3	-13	-25	-26	1.000	1.000	0.994
Day 27	-108	-237	-146	**0.001**	**0.000**	**0.000**
Day 63	-213	-148	-101	**0.000**	**0.000**	**0.001**
Day 104	-135	-136	-76	**0.002**	**0.000**	0.110
Day 160	-48	-38	-22	0.825	0.883	0.996
Ultidril base fluid						
Day 3	-14	-12	-13	0.990	0.989	0.995
Day 27	-80	-70	-50	0.131	0.189	0.227
Day 63	-41	-38	-31	0.851	0.636	0.729
Day 104	-7	-32	-32	1.000	0.876	0.872
Day 160	-55	-49	-50	0.438	0.389	0.344
Ultidril cuttings						
Day 3	-6	-14	-33	1.000	0.552	0.814
Day 27	-70	-84	-56	0.290	**0.045**	0.103
Day 63	-59	-54	-48	0.567	0.596	0.275
Day 104	-28	-55	-43	0.977	0.226	0.558
Day 160	-42	-34	-27	0.769	0.829	0.947

Significant differences between controls and treated chambers were only found at 15 and 25 mm depth in the Petrofree chamber on day 104 (Table 13). However, Figure 12 showed small but persistent negative deviations in both Ultidril treatments and the ester treatment. Statistical analyses for the entire time series (Table 15) showed that the mean negative deviation of .118-121 pH-units at 15-25mm depth in the Petrofree chamber was, significant at >97%. In the Ultidril treatments, however, the mean negative deviations of .058-.064 pH-units for the entire sampling period, were not significant.

The highest redox potentials were observed in the chamber water and surface layer of the sediments. The range of 267-355 mV of mean E_h in the water in all chambers was not much different from the mean potentials observed at 5mm depth in the control sediment (Table 12). In the Petrofree chambers the E_h dropped to low values throughout

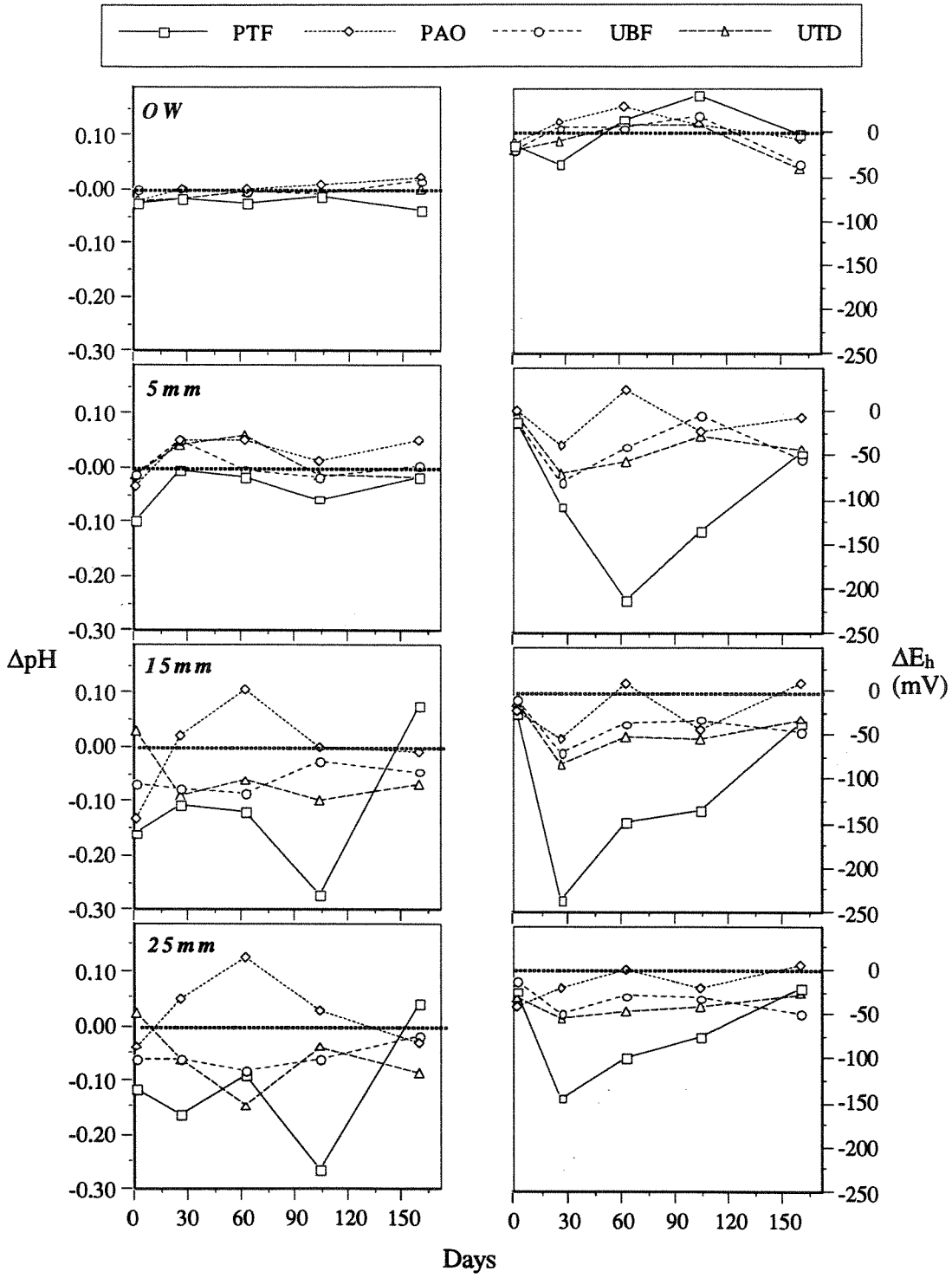


Figure 12. Variation with time of deviations of pH and Eh in treated relative to control chambers. Observations were taken in the chamber water (OW) and at 5mm, 15mm and 25mm depth in the sediment.

Table 15. Mean difference of pH and redox potentials in treated versus control sediments during the entire sampling period (day 0-160). Right-hand columns show the probability of each difference. Bold numbers highlight significant differences.

	Numeric difference				Probability (p)			
	OW	5 mm	15mm	25mm	OW	5mm	15mm	25mm
pH								
Novadril	0.000	0.027	-0.005	0.026	1.000	0.801	1.000	0.963
Petrofree	-0.026	-0.041	-0.118	-0.121	0.606	0.443	**0.010**	**0.022**
UBF	-0.001	0.003	-0.062	-0.058	1.000	1.000	0.201	0.379
UTD	-0.012	0.011	-0.059	-0.064	0.916	0.978	0.244	0.284
Eh (mV)								
Novadril	5.6	-9.3	-22.1	-16.1	0.983	0.984	0.559	0.623
Petrofree	-3.2	-112.9	-116.4	-74.9	0.998	**0.000**	**0.000**	**0.000**
UBF	-8.5	-44.5	-45.2	-39.1	0.855	**0.021**	**0.003**	**0.001**
UTD	-11.0	-41.0	-47.9	-41.3	0.691	**0.042**	**0.001**	**0.000**

the 30-111 days period (Figure 12). The lowest single value of -131mV was measured on day 27, below a black area. In the Ultidril treatments, E_h decreased during the 3-27 days time interval, to a level about 50 mV below the E_h in the control sediment. This level was maintained throughout the experimental period.

Table 14 shows that apart from the significance of the negative deviations in the Petrofree chambers 27-104 days after addition of cuttings, a significant negative deviation was only observed at 15 mm depth in the Ultidril chambers on day 28. Considering, however, the entire experimental period, the persistent negative deviations of 39.1-47.9 mV(Table 15), were significant at the 95% confidence level. Thus, the deposition of Ultidril olefins produced a moderate deviation of the redox potential in the sediment. The deviation was significant at the 95% confidence level and persisted in the sediment for at least 160 days after deposition of the cuttings.

4.4.3 Composition of benthic communities by the end of the experiment

The benthic fauna was collected by washing the top 10 cm of the sediments on a 1 mm mesh size sieve. The samples were preserved in formalin, and sorted into the main taxonomic groups, Polychaeta, Crustacea and Mollusca. In some cases, animals were further identified only to family level. 15 different taxa (species) were identified and up to 446 individuals were found in each chamber. Reflecting the different origins of the top and bottom layers in the chambers, species characteristic for deep (50-200m) clay sediments as well as intertidal species were observed present.

Species lists are given in Appendix . Community parameters and mean body weight of *Nereis diversicolor* is shown in Table 16 and plotted against the total sediment oxygen consumption for the experimental period in Figure 13.

The chambers were dominated by high numbers (59-301 individuals per chamber) of the polychaete *Nereis diversicolor* and the small snails *Hydrobia ulvae & ventrosa.* (51-189 individuals per chamber).

Table 16. Body weight (wet wght.) of *Nereis diversicolor* and numbers of taxa and individuals determined in each chamber by the end of the experiment. The number of individuals in the two dominant groups *Nereis* and *Hydrobia* was subtracted from total number of individuals to obtain the number of individuals of "rare" species.

	Taxa (nos.)	Number of individuals			Body wght. Nereis ($mg \cdot ind.^{-1}$)
		All species	Nereis and Hydrobia	Rare species	
CON 1	8	(99)	(81)[2]	18	10
CON 4	6	268	249	19	12
PAO 6	8	244	223	21	16
PTF 3	7	381	347	34	31
UTD 5	6	439	419	20	19
UTD 8	7	446	423	23	24
UBF 2	6	412	392	20	27
UBF 7	7	155	140	25	21

[2] Number of Hydrobia were not counted in this sample.

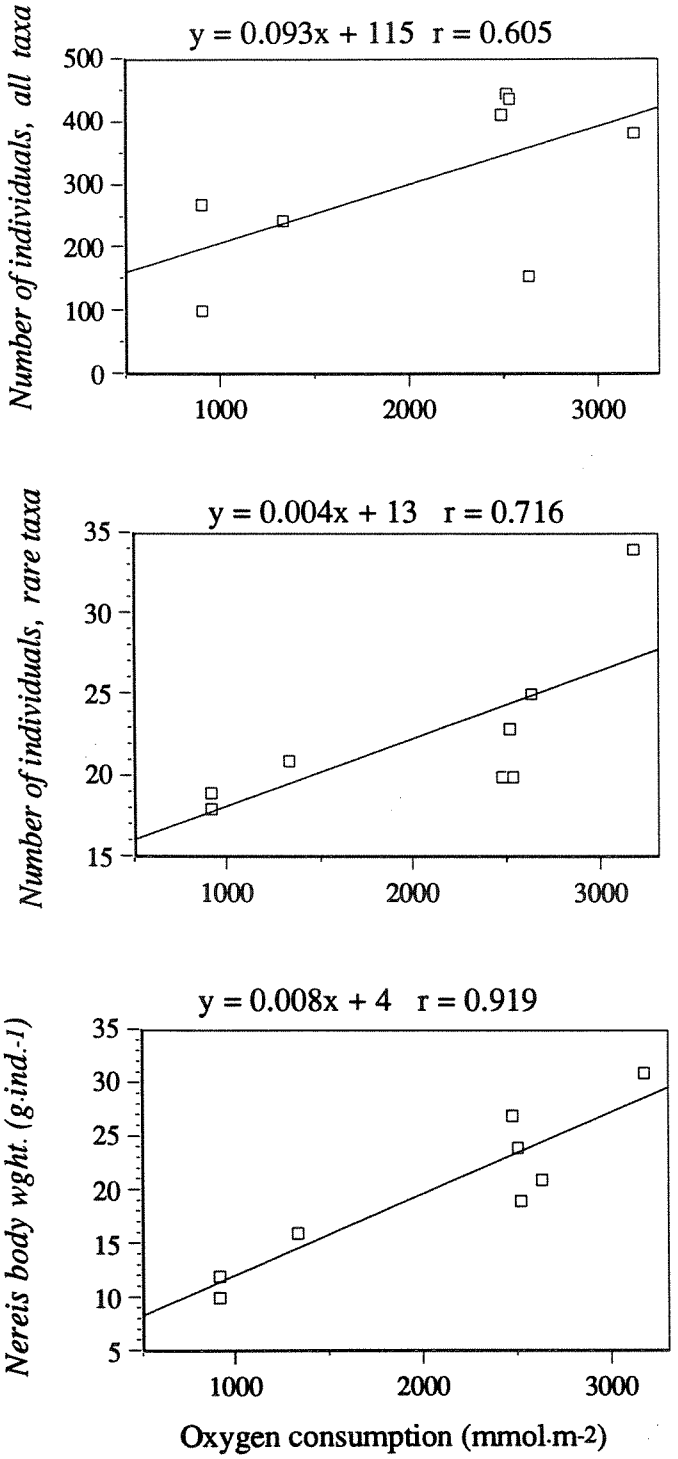


Figure 13. Correlation between total sediment oxygen consumption and macrofauna parameters determined on day 176.

Many individuals of the latter group were observed also in control chamber 1, but because of difficulties in distinction between dead and living individuals by the time of sampling, the group was not quantified in this sample. Thus, the total number of individuals found in control 1 was highly underestimated. Both of the dominant groups were present in relative low numbers in UBF 7. By subtraction of the two most dominant groups, the remaining "rare" number of individuals in CON 1 as well as in UBF 7, agreed well with the range observed in the other chambers (Table 16).

Nereis diversicolor is known for high tolerance in low-oxic environments and rapid colonisation of areas with an increased supply of nutrients or digestible organic matter. The populations present in the benthic chambers, were composed mainly of juvenile species. However, a remarkable difference between the size of the individuals in the various treatments was observed. Thus, the mean wet weight ranged from 11 mg in the control chambers to 31 mg in the Petrofree chamber (Table 16).

Correlation between various macrofauna parameters and the total oxygen consumption accumulated over the experimental period is shown in Figure 13. Curve equations calculated by linear regression analyses are shown on top of each diagram along with the correlation coefficient, r. For eight observations and six degrees of freedom, the critical value of r is 0.71 at 95% confidence level (Pearson and Hartley, 1966). Thus, the correlation between total number of individuals and sediment oxygen consumption was not significant. This correlation was neither significant when omitting CON 1, in which Hydrobia was not counted.

However, the correlation with the number of individuals of the rare species, was found to be significant at 95% and the correlation with body weight was significant at 99% (critical r=0.83). The occurrence of fewer, but larger individuals of *Nereis* in the Petrofree chamber (see Table 16 and right-hand symbol in Figure 12) may have resulted from negative effects on recruitment or survival during the most intensive degradation period when redox potentials dropped to very low values in this sediment (Figure 12). The macrofauna revealed no negative effects of the moderate lowering of the redox potentials observed in the Ultidril chambers.

5. CONCLUSIONS

1. Technically, the test performed very well. No severe problems occurred neither in test preparation, maintenance, sample collection nor analyses.
2. GC/MS-analyses confirmed that the supplied sample of liquid Ultidril base fluid was a mixture of two unsaturated olefin compounds with the chemical formulae $C_{14}H_{28}$ and $C_{16}H_{32}$.
3. Negligible differences were found between chambers treated with Ultidril mud on cuttings sampled from off-shore drilling operations and chambers treated with non-contaminated sediment soaked with Ultidril base fluids.
4. Independent parameters such as

- decrease of concentration of drill fluids in the sediment,
- sediment oxygen consumption,
- visual effects on sediment surface,
- deviations of pH and redox potentials from control sediments,
- number of individuals of rare species and
- body size of the dominant polychaetes,

were consistent in showing biodegradation rates and environmental effects of Ultidril olefins intermediate between the two reference products Novadril II olefins and Petrofree esters .

5. A range of half-lives of 36-50 days and a mean of 43 days was found by exponential regression analyses of the decrease of concentration of olefins in the four chambers treated with Ultidril.
6. Of the two Ultidril components, the tetradecene degraded faster than the hexadecene.
7. The half-life of Ultidril olefins was intermediate between the half-life of 20 days for the Petrofree ester and 127 days for the Novadril II olefins.
8. The DF:Ba ratio as well as the oxygen consumption rates showed that biodegradation of the Novadril II olefins ceased between 62 and 100 days after deposition of the cuttings.

9. By the termination of the experiment, less than 0.01% of the initial concentration of Petrofree esters were present in the sediment as compared to 3-10% of the Ultidril olefins and 38% of the Novadril II olefins.
10. By combining conclusions 8 and 9 it follows that Novadril II base fluid deposits may remain present in sediments for periods of time much longer than the time predicted by the estimated half-life of 127 days.
11. Mass balance calculations indicated that 23%, 80% and 44-60%, respectively, of the initial presence of Novadril II, Petrofree and Ultidril base fluid carbon, had been completely mineralised to CO_2 during the test period. Because oxygen consumption in the chamber treated with the two latter drill fluids were still higher than the oxygen consumption in control chambers, the mineralisation fractions would continue to increase in a prolonged experiment.
12. The appearance of dead mussels and coloured patches on the sediment surface during the 27-100 days period, indicated that the treatments had affected the pore water environment in the Ultidril and Petrofree chambers more than in the control and Novadril chambers.
13. For the entire sampling period of 3-160 days, significant difference was found between the pH at 15 and 25 mm sediment depth in control chambers and the chamber treated with Petrofree esters. No other chambers showed any significant deviation of pH.
14. The redox potentials were significantly lowered at all depths (5, 15 and 25mm) in the Ultidril chambers as well as in the Petrofree chamber. The mean negative deviation for the experimental period was 75-119 mV in the Petrofree chamber and 39-48 mV for the Ultidril treatments. The corresponding negative deviation of 9-22 mV in the Novadril chamber was not significant at the 95% confidence level.
15. Analyses of the benthic fauna on day 176, showed that the total number of 155-446 individuals in each chamber were clearly dominated by the polychaete *Nereis diversicolor* and the small snails *Hydrobia ulvae & ventrosa.*
16. Compared with control chambers and chambers treated with Novadril olefins, the number of individuals was higher in the chamber treated with Petrofree esters and in three of the four chambers treated with Ultidril olefins.
17. The mean body weight of *Nereis* ranged from 10-12 mg in control sediments, via 16 mg in the Novadril chamber and 19-27 mg in the Ultidril chambers to 31 mg in the Petrofree chamber.
18. Significant correlation were found between the total sediment oxygen consumption and, respectively, total number of rare species (r=0.716) and body weight of the most dominant polychaete (r=0.919).

19. The occurrence of fewer, but larger individuals of *Nereis* in the Petrofree chamber, may have resulted from negative effects on recruitment or survival during the most intensive degradation period.
20. The macrofauna analyses revealed no clear evidence of negative effects of the moderate lowering of the redox potentials observed in the Ultidril chambers.

6. REFERENCES

Bakke, T., J.S.Grey and L.O.Reiersen, 1989a. Monitoring in the Vicinity of Oil and Gas Platforms: Environmental Status in the Norwegian Sector in 1987-1989. Proceedings 1st Int. Symposium on Oil and Gas Exploration and Production Waste, 623-633.

Bakke, T., J.A.Berge, M.Schaanning, G.M.Skeie and F.Oreld, 1989b. Effects of Low-aromatic Drill Cuttings on an Enclosed Deepwater Sediment Community. In *Drilling Wastes*, eds. F.R.Engelhardt, J.P.Ray and A.H.Gillam, Elsevier Applied Science, pp495-519.

Bakke, T. and M.Laake, 1991. Tests on degradation of a new drill mud type under natural conditions. NIVA report no 2538, 19pp,+ addendum, appendix.

Bakke T., J.S.Grey, R.G.Lichtenthaler og K.H.Palmork, 1993. Miljøundersøkelser rundt petroleumsinstallasjoner på norsk kontinentalsokkel. Rapport for 1991. SFT, november 1993.

Bakke T., J.S.Grey, R.G.Lichtenthaler og K.H.Palmork, 1994. Miljøundersøkelser rundt petroleumsinstallasjoner på norsk kontinentalsokkel. Rapport for 1992.

Daan, R., K.Booij, M.Mulder and E.M. van Weerle, 1995. A study of the Environmental Effects of a Discharge of Drill Cuttings Contaminated with Ester Based Muds in the North Sea. Netherlands Institute for Sea Research, *NIOZ-rapport* 1995-2, 50pp.

Dicks, B., T.Bakke, and I.M.Dickson, 1986/87. Oil Exploration and Production: Impact on the North Sea. *Oil & Chemical Pollution*, 3, 289-306.

Gislasson, H., J.Gray, U.Grimås, W.Hickel, R. Stagg and F.v.d.Falk, 1993. Man's impact on ecosystems. In *North Sea Quality Status Report, 1993*. Oslo and Paris Commissions, London. pp80-99.

Gray, J.S., K.R.Clarke, R.M.Warwick and G.Hobbs, 1990. Detection of initial effects of pollution on mArine benthos: an example from Ekofisk and Eldfisk oilfields, North Sea. *Mar.Ecol.Prog. Ser.*, 66, 285-299.

Kaarstad, I., T.Berg and R.Jacques, 1994. Miljøundersøkelsen av det marine miljø på Statfjordfeltet 1993. IKU Petroleumsforskning a.s., Rapport 93.180, 321pp.

Laake, M., T.Bakke and M.Schaanning, 1992. "Joint Study of Environmental Impact of Aquamul Cuttings" & "Test on Degradation and Environmental of Thermal Treated Oily Cuttings under Natural Conditions". NIVA report no 2744. 61pp, appendix.

Olsgaard, F. 1994. Pollution-induced disturbance in marine soft-bottom communities. Dr.Scient Thesis, University of Oslo, 1994.

Pearson, E.S. and H.O.Hartley, 1966. "Biometrica Tables for Statisticians" Vol.1, 3rd ed., Cambridge Univ. Press, London and New York.

Reiersen, L.O., J.S.Grey, K.H.Palmork and R.Lange, 1989. Monitoring in the vicinity of oil and gas platforms; results from the Norwegian sector of the North Seaand recommended methods for forthcoming surveillance. In Drilling Wastes (F.R. Engelhardt, J.P.Ray and A.H.Gilham, Eds.) Elsevier Applied Science, 91-117.

Schaanning, M.T. and M.Laake, 1993. "Test on degradation of Novadril drill mud on cuttings under simulated seabed conditions". NIVA report no.2866. 72 pp.

Schaanning, M.T., 1994. "Test on Degradation of AQUAMUL BII Drill Mud on Cuttings under Simulated Seabed Conditions". NIVA report no.3092. 42pp + appendix.

Schaanning, M.T. 1995. "Environmental Fate of Synthetic Drilling Fluids from Offshore Drilling Operations". NIVA report no.3178. 62pp + appendix.

Schaanning, M.T. 1995b. "Evaluation of Overall Marine Impact of the Novadril Mud Systems". NIVA report no.3260. 31pp.

Smith, J. and G.Hobbs, 1993. Ula well site 7/12-9 Environmental survey 1992. A report to SINTEF SI from the Field Studies Council Research Centre. March 1993.

Zevenboom, W., M.Robson, L.Massie and L.O.Reiersen, 1993. *Environmental effects of offshore mining discharges.* A contribution to the 1993 Quality Status Report of the North Sea. Oslo and Paris Commissions, London.

ZoBell, C.E., 1946. Studies of Redox Potential of Marine Sediments. *Bull. Am. Ass. Petrol. Geol.*, 30: 477-513.

7. APPENDIX I: Tables of results

Table AI.1. Recorded values of E_h and pH in chamber water (OW) and at three depths in the sediment.

			pH				Eh(mV)			
Chamber		Loc	OW	5 mm	15 mm	25 mm	OW	5 mm	15 mm	25 mm
Day 2										
CON	1	1	7.87	7.87	7.79	7.62	364	364	193	142
CON	1	2	7.83	7.84	7.69	7.48	308	317	214	169
CON	1	3	7.83	7.85	7.75	7.50	307	318	254	169
CON	4	1	7.83	7.84	7.61	7.44	349	348	186	142
CON	4	2	7.83	7.85	7.85	7.66	318	327	246	188
CON	4	3	7.84	7.81	7.64	7.51	320	244	159	120
UTD	5	1	7.81	7.83	7.72	7.52	314	320	227	132
UTD	5	2		7.83	7.77	7.52	309	312	180	108
UTD	5	3	7.81	7.83	7.70	7.46	312	318	179	104
UTD	8	1	7.82	7.84	7.82	7.58	299	305	221	156
UTD	8	2	7.82	7.82	7.74	7.61	308	310	192	123
UTD	8	3	7.82	7.83	7.75	7.65	307	316	172	107
UBF	2	1	7.86	7.77	7.67	7.50	-	-	232	187
UBF	2	2	7.86	7.86	7.75	7.51	303	304	234	205
UBF	2	3	7.83	7.84	7.72	7.52	309	311	172	121
UBF	7	1	7.83	7.84	7.60	7.47	315	322	183	117
UBF	7	2	7.83	7.83	7.62	7.45	307	293	153	97
UBF	7	3	7.81	7.83	7.55	7.38	298	300	205	125
PAO	6	1	7.81	7.77	7.69	7.59	316	320	197	115
PAO	6		7.83	7.83	7.50	7.36	314	318	192	101
PAO	6	3	7.81	7.83	7.58	7.54	310	315	169	120
PTF	3	1	7.81	7.84	7.60	7.53	324	330	203	145
PTF	3	2	7.81	7.65	7.52	7.39	306	291	173	121
PTF	3	3	7.81	7.74	7.56	7.33	305	299	175	120
Day 27										
CON	1	1	7.87	7.61	7.58	7.52	270	268	208	159
CON	1	2	7.85	7.85	7.61	7.47	281	283	176	106
CON	1	3	7.88	7.86	7.73	7.55	283	290	204	152
CON	4	1	7.91	7.91	7.84	7.61	331	338	249	187
CON	4	2	7.86	7.86	7.72	7.60	323	332	242	188
CON	4	3	7.88	7.88	7.74	7.70	325	313	223	144
UTD	5	1	7.87	7.89	7.63	7.58	295	293	149	122
UTD	5	2	7.85	7.86	7.60	7.49	290	207	141	109
UTD	5	3	7.85	7.87	7.57	7.50	289	288	136	94
UTD	8	1	7.86	7.88	7.69	7.57	301	215	110	74
UTD	8	2	7.86	7.86	7.63	7.57	286	210	134	97
UTD	8	3	7.84	7.86	7.55	7.37	288	190	130	106
UBF	2	1	7.91	7.91	7.74	7.52	321	282	184	142
UBF	2	2	7.88	7.89	7.55	7.55	320	243	142	110
UBF	2	3	7.88	7.88	7.53	7.44	319	208	129	100
UBF	7	1	7.85	7.86	7.69	7.55	285	238	167	126
UBF	7	2	7.86	7.88	7.63	7.53	297	199	142	93
UBF	7	3	7.86	7.86	7.60	7.48	294	175	119	68
PAO	6	1	7.88	7.88	7.74	7.73	291	259	146	161
PAO	6	2	7.86	7.86	7.66	7.62	332	244	169	136
PAO	6	3	7.88	7.90	7.76	7.52	320	294	169	112
PTF	3	1	7.88	7.78	7.66	7.49	-	222	82	87

PTF	3	2	7.85	7.85	7.51	7.38	258	120	-131	-29
PTF	3	3	7.84	7.83	7.61	7.36	276	245	-11	-27
Day 63										
CON	1	1	7.83	7.78	7.59	7.38	263	273	152	127
CON	1	2	7.83	7.79	7.59	7.53	316	322	182	139
CON	1	3	7.81	7.84	7.61		317	335	217	170
CON	4	1	7.80	7.73	7.57	7.43	368	376	217	172
CON	4	2	7.80	7.83	7.57	7.48	345	363	230	180
CON	4	3	7.83	7.59	7.53	7.50	336	371	253	198
UTD	5	1	7.82	7.82	7.52	7.24	320	301	173	130
UTD	5	2	7.80	7.82	7.54	7.46	333	271	172	137
UTD	5	3	7.81	7.82	7.47	7.22	320	269	162	123
UTD	8	1	7.82	7.83	7.64	7.39	350	322	140	90
UTD	8	2	7.80	7.81	7.39	7.29	333	323	166	119
UTD	8	3	7.81	7.82	7.52	7.28	328	199	116	100
UBF	2	1	7.81	7.74	7.52	7.46	343	263	145	132
UBF	2	2	7.81	7.81	7.54	7.52	319	316	168	139
UBF	2	3	7.82	7.58	7.40	7.28	325	704*	258	169
UBF	7	1	7.81	7.78	7.47	7.43	337	340	125	106
UBF	7	2	7.80	7.83	7.52	7.41	316	331	176	128
UBF	7	3	7.82	7.77	7.48	7.19	326	246	154	129
PAO	6	1	7.80	7.80	7.62	7.56	366	369	212	164
PAO	6	2	7.84	7.84	7.65	7.51	348	361	207	160
PAO	6	3	7.80	7.80	7.77	7.69	347	364	227	167
PTF	3	1	7.81	7.66	7.28	7.19	423	248	183	173
PTF	3	2	7.78	7.76	7.45	7.42	342	39	5	11
PTF	3	3	7.78	7.80	7.64	7.50	248	94	-6	5
Day 104										
CON	1	1	7.93	7.92	7.74	7.58	280	288	222	164
CON	1	2	7.94	7.94	7.75	7.62	296	312	199	127
CON	1	3	7.92	7.93	7.61	7.54	306	305	274	189
CON	4	1	7.94	7.94	7.86	7.68	346	360	234	149
CON	4	2	7.92	7.94	7.88	7.78	334	347	219	154
CON	4	3	7.92	7.96	7.83	7.63	326	348	206	132
UTD	5	1	7.91	7.91	7.66	7.57	322	256	174	127
UTD	5	2	7.92	7.92	7.71	7.58	326	317	202	123
UTD	5	3	7.92	7.90	7.61	7.55	300	319	192	142
UTD	8	1	7.91	7.93	7.70	7.69	356	287	179	120
UTD	8	2	7.92	7.95	7.79	7.72	317	315	142	69
UTD	8	3	7.94	7.94	7.60	7.48	315	301	134	78
UBF	2	1	7.92	7.93	7.89	7.60	375	378	184	163
UBF	2	2	7.94	7.95	7.73	7.52	347	360	190	140
UBF	2	3	7.92	7.93	7.72	7.47	331	337	217	136
UBF	7	1	7.90	7.92	7.70	7.54	311	255	172	141
UBF	7	2	7.89	7.87	7.76	7.73	323	337	236	17
UBF	7	3	7.93	7.93	7.70	7.58	312	252	166	129
PAO	6	1	7.93	7.96	7.78	7.74	315	317	184	137
PAO	6	2	7.94	7.95	7.72	7.66	327	335	195	141
PAO	6	3	7.93	7.94	7.83	7.60	330	258	162	119
PTF	3	1	7.95	7.87	7.39	7.30	440	168	127	115
PTF	3	2	7.89	7.88	7.58	7.47	290	265	157	129

PTF	3	3	7.90	7.89	7.54	7.34	336	141	-14	-15
Day 160										
CON	1	1	7.88	7.89	7.72	7.63	342	219	172	126
CON	1	2	7.93	7.93	7.76	7.75	326	262	192	139
CON	1	3	7.94	7.94	7.63	7.49	322	319	172	145
CON	4	1	7.97	7.94	7.63	7.54	360	239	168	134
CON	4	2	7.97	7.87	7.86	7.86	315	277	178	133
CON	4	3	7.97	7.97	7.06	7.57	278	306	189	152
UTD	5	1	7.90	7.92	7.65	7.60	333	250	159	140
UTD	5	2	7.91	7.84	7.58	7.50	231	252	169	124
UTD	5	3	7.94	7.86	7.60	7.42	281	207	144	114
UTD	8	1	7.97	7.97	7.61	7.52	329	217	124	85
UTD	8	2	7.98	7.92	7.56	7.52	231	195	142	118
UTD	8	3	7.94	7.92	7.78	7.75	301	249	131	87
UBF	2	1	7.97	7.86	7.63	7.56	335	299	179	88
UBF	2	2	7.96	7.96	7.59	7.56	303	235	54	17
UBF	2	3	7.97	7.96	7.44	7.39	231	257	200	154
UBF	7	1	7.94	7.94	7.68	7.64	320	178	123	93
UBF	7	2	7.94	7.93	7.88	7.87	276	131	80	64
UBF	7	3	7.96	7.90	7.71	7.72	271	194	144	114
PAO	6	1	7.96	7.98	7.72	7.66	311	299	213	163
PAO	6	2	7.97	7.97	7.63	7.50	316	229	152	125
PAO	6	3	7.97	7.97	7.72	7.67	318	260	190	136
PTF	3	1	7.95	7.92	7.85	7.72	348	236	127	97
PTF	3	2	7.88	7.90	7.78	7.71	303	248	169	138
PTF	3	3	7.88	7.90	7.70	7.61	308	182	125	113

Table AI.2. Concentration of barium and drilling fluids and drilling fluid:Barium ratios in the material added on day zero.

	Ba	DF	DF:Ba
	$mg \cdot kg^{-1}$		
Ultidrill cuttings sample	82 000	97 000	1.18
Control sed. soaked with Ultdidril base fluid	1 090	265 000	243
Petrofree cuttings sample	51 000		1.19
Novadril II cuttings sample	41 000	56 300	1.37

Table AI.3. Concentration of barium and drilling fluids and drilling fluid:Barium ratios in all sediment samples. Excess barium was calculated by subtraction of mean concentration in control sediment.

		Barium		Ba-excess	Drilling fluid		DF:Ba-ratio	
		$mg \cdot kg^{-1}$	$mg \cdot cm^{-2}$	$mg \cdot cm^{-2}$	$mg \cdot kg^{-1}$	$\cdot cm^{-2}$	absolute	excess
Day 3								
PTF	3	1 450	4.399	1.82	803	2.44	0.55	1.34
PAO	6	1 420	4.280	1.72	570	1.72	0.40	1.00
UTD	5	1 630	5.279	2.53	773	2.50	0.47	0.99
UTD	8	2 000	6.132	3.53	1 110	3.40	0.56	0.97
UBF	2	900	2.613	-	1 150	3.34	1.28	-
UBF	7	830	2.503	-	888	2.68	1.07	-
Day 27								
PTF	3	1 510	5.062	2.21	697	2.34	0.46	1.06
PAO	6	1 290	4.389	1.50	419	1.43	0.32	0.95
UTD	5	1 570	5.368	2.46	583	1.99	0.37	0.81
UTD	8	1 590	5.431	2.53	453	1.55	0.28	0.61
UBF	2	880	2.913	-	773	2.56	0.88	-
UBF	7	820	2.784	-	670	2.27	0.82	-
Day 62								
UTD	5	1 490	5.252	2.26	315	1.11	0.21	0.49
UTD	8	1 680	5.520	2.73	509	1.67	0.30	0.61
UBF	2	880	2.856	-	733	2.38	0.83	-
UBF	7	850	2.820	-	344	1.14	0.40	-
PAO	6	1 340	4.531	1.66	336	1.14	0.25	0.69
PTF	3	1 550	5.314	2.40	435	1.49	0.28	0.62
Day 100								
PTF	3	1 540	5.322	2.38	61	0.21	0.04	0.09
PAO	6	1 370	4.648	1.76	241	0.82	0.18	0.46
UTD	5	1 680	5.606	2.77	289	0.96	0.17	0.35
UTD	8	1 540	5.188	2.32	253	0.85	0.16	0.37
UBF	2	850	2.903	-	442	1.51	0.52	-
UBF	7	840	2.901	-	260	0.90	0.31	-
Day 160								
PTF	3	1 450	4.589	1.499	3	0.008	0.002	0.006
PAO	6	1 360	4.911	1.479	242	0.702	0.178	0.475
UTD	5	2 120	6.122	3.088	198	0.481	0.093	0.156
UTD	8	1 610	4.747	1.784	74	0.174	0.046	0.097
UBF	2	870	2.925	-	103	0.242	0.118	-
UBF	7	820	2.874	-	81	0.199	0.099	-
Day 176								
PTF	3	1 430	4.945	2.006	3	0.011	0.002	0.005
PAO	6	1 220	4.029	1.222	200	0.660	0.164	0.541
UTD	5	1 490	4.854	2.085	46	0.150	0.031	
UTD	8	1 230	3.984	1.231	30	0.097	0.024	0.079
UBF	2	870	2.898	-	102		0.117	-
UBF	7	830	2.795	-	34	0.114	0.041	-

Table AI.4. Sediment oxygen consumption in each chamber ($\mu molO_2.m^{-2}.h^{-1}$).

Date	Day	1-CON	4-CON	5-UTD	8-UTD	2-UBF	7-UBF	6-PAO	3-PTF
21.11.94	5	161	294	884	880	619	887	453	759
24.11.94	8	366	334	975	-	562	663	684	848
01.12.94	15	305	308	885	805	677	915	696	1148
06.12.94	20	264	259	738	789	706	704	532	919
09.12.94	23	358	340	657	860	775	841	660	1231
12.12.94	26	227	189	410	517	443	556	257	934
13.12.94	27	173	93	679	644	591	644	441	1071
16.12.94	30	259	218	579	542	552	580	435	839
20.12.94	34	224	217	533	501	531	603	292	1075
23.12.94	37	284	297	784	748	731	806	624	1256
27.12.94	41	216	175	594	625	566	654	349	1189
30.12.94	44	135	-8	420	346	167	461	-	966
03.01.95	48	314	267	861	875	835	904	584	1423
06.01.95	51	225	333	576	763	868	977	311	1365
10.01.95	55	140	167	660	782	533	680	210	1044
13.01.95	58	232	160	542	607	504	548	159	849
16.01.95	61	318	420	1002	1069	1077	901	706	1275
20.01.95	65	143	91	648	681	894	672	155	944
27.01.95	72	-	-	-	-	-	-	-	-
01.02.95	77	186	266	665	521	630	753	537	494
03.02.95	79	178	193	589	645	602	585	249	644
07.02.95	83	254	275	770	804	780	806	414	878
10.02.95	86	204	201	634	645	646	646	266	742
14.02.95	90	226	189	601	652	610	616	250	701
17.02.95	93	311	212	681	620	649	661	249	544
22.02.95	98	172	180	470	522	607	559	180	664
28.02.95	104	108	55	508	488		514	216	526
02.03.95	106	135	173	612	597	580	661	194	569
07.03.95	111		219	606	625	594	690	310	741
10.03.95	114	239	194	580	502	479	523	196	675
14.03.95	118	119	162	574	537	524	520	239	593
17.03.95	121	116	153	489	470	468	514	174	581
21.03.95	125	202	243	604	585	631	612	296	688
24.03.95	128	229	232	643	604	614	597	309	664
28.03.95	132	142	257	436	343	402	248	75	494
31.03.95	135	285	154	428	536	421	517	127	509
04.04.95	139	268	266	622	543	645	602	335	663
07.04.95	142	210	234	453	500	531	535	162	538
12.04.95	147	251	214	509	482	551	616	133	610
19.04.95	154	217	206	374	503	458	548	186	434
21.04.95	156	235	235	382	315	473	548	98	377
25.04.95	160	176	-	469	425	463	484	79	401
28.04.95	163	305	324	679	614	767	781	324	718
02.05.95	167	231	205	484	439	542	427	277	485
05.05.95	170	185	169	370	362	448	285	176	343
09.05.95	174	238	213	491	435	524	380	292	454

8. APPENDIX II: Analyses of benthic fauna from experimental tanks at Solbergstrand, Akvaplan-niva

Table AII.1. Number of macrofauna individuals, number of taxa and the A/S (individuals:taxa) ratio in each chamber by the end of the experiment.

Species	1 -CON	2 - UBF	3 - PTF	5 - UTD	6 - PAO	7 - UBF	7 - CON	8 - UTD
Phylum Nemertini								
Nemertini indet						1		
Phylum Annelida								
Class Polychaeta								
Capitella capitata					1			
Goniada maculata						1		
Myriochele oculata	1							
Nephtys incisa			1					
Nereis irrorata	81	272	158	301	163	59	198	234
Nereis virens				1				
Polychaeta indet	1							
Class Oligochaeta								
Oligochaeta indet	3	2	8	11	2	5	6	5
Phylum Crustacea								
Calanoida indet	2	9			2	1	5	8
Phylum Mollusca								
Cardium edule	1		3	2	2			7
Hydrobia ulvae & ventrosa		120	189	118	60	72	51	189
Macoma baltica	3	3	5		1	2	4	1
Mya sp	7	6	17	6	12	15	4	2
Mytilus edulis								
Rissoa membranacea								
PhylumSipunculida								
Sipunculida indet					1			
Phylum Nemertini								
Nemertea indet								
Total no. taxa	8	6	7	6	8	7	6	7
Total no. individuals	99	412	381	439	244	155	268	446
A/S	12	69	54	73	31	22	45	64

Table AII.2. Total wet weight, number of individuals and mean body biomass of *Nereis diversicolor* in each chamber by the end of the experiment.

	Wet wght. (g)	Number	Mean size (g)
1 -CON	0.80	81	0.0099
2 - UBF	7.26	272	0.0267
3 - PTF	4.93	158	0.0312
5 - UTD	5.71	301	0.0190
6 - PAO	2.67	163	0.0164
7 - UBF	1.23	59	0.0208
7 - CON	2.41	198	0.0122
8 - UTD	5.66	234	0.0242

9. APPENDIX III: Report on chemical analyses, SINTEF-Industrial Chemistry

REPORT

STF27 F95029

Classification: Confidential

Biodegradation of Ultidril Base Fluid and Drilling Mud on Cuttings Deposited in Benthic Chambers

SINTEF Industrial Chemistry

June 1995

SINTEF

SINTEF

SINTEF

Address: Postboks 124 Blindern,
N-0314 Oslo, NORWAY
Location: Forskningsveien 1
Telephone: +47 22 06 73 00
Fax: +47 22 06 73 50
Telex: 71 536 SI N

Enterprise No.: 948007029

SINTEF REPORT

TITLE

Biodegradation of Ultidril base fluid and drilling mud on cuttings deposited in benthic chambers

AUTHOR(S)

Frøydis Oreld

CLIENT(S)

NIVA

REPORT NO.	CLASSIFICATION	CLIENT'S REF.	
STF27 F95029	Confidential	Morten Schaanning	
CLASS. FRONT PAGE	ISBN	PROJECT NO.	NO. OF. PAGES/APPENDICES
Confidential		270261.00	15
ELECTRONIC FILE CODE		DISCIPLINARY RESPONSIBILITY	
REPORT.DOC		Frøydis Oreld	Frøydis Oreld
FILE CODE	DATE	RESPONSIBLE SIGNATURE	
5ultidrl.doc	1995-06-20	Nina Gjøs	Nina Gjøs

ABSTRACT

The report presents the results of determination of Ultidril tetra- and hexadecene isomers, Novasol II eicosane isomers, Petrofree ester and barium content in sediment samples.

KEYWORDS	ENGLISH	NORWEGIAN
GROUP 1	Chemistry	Kjemi
GROUP 2	Analysis	Analyse
SELECTED BY AUTHOR(S)	Drilling fluids	Borevæsker
	Barium	Barium
	Degradation	Nedbrytning

TABLE OF CONTENTS

1. INTRODUCTION page 3

2. CHEMICAL ANALYSES - METHODS page 4

2.1 Analytical procedure page 4

2.2 Quality assurance programme page 6

3. RESULTS AND DISCUSSION page 8

3.1 Ultidril page 8

3.2 Novasol II and Petrofree page 12

3.3 Barium page 12

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.

"Ultidril" is a new drill mud type where alkene compounds are substitutes for base oil. Tests to investigate the degradability and environmental effects of Ultidril base fluid and drilling mud have been performed at the NIVA Marine Research Station at Solbergstrand.

The chemical analyses of sediment samples with regard to the content of Ultidril alkene 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 Novasol II 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.

Project team at SINTEF Industrial Chemistry:

Project Responsible: Nina Gjøs
Project Manager: Frøydis Oreld

Ultidril, Novasol, Petrofree analyses:
Anne Norsted
Line T. Sunde
Tone Øfsti

Barium analyses:
Ingegerd Rustad

2. CHEMICAL ANALYSES - METHODS

2.1 ANALYTICAL PROCEDURE

2.1.1 Identity of Ultidril

A sample of Ultidril base fluid was available from Schlumberger Dowell. Information from Morten Schaanning, NIVA on phone 1995-01-19, was that Ultidril was stated to consist of hexadecene in a mixture with some tetra- and octadecene.

To confirm the chemical identity, a sample of the received Ultidril liquid was analysed by gas chromatography-mass spectrometry (GC/MS). The analysis confirmed that the liquid Ultidril consists of a mixture of tetradecene with the chemical formula $C_{14}H_{28}$ and hexadecene with the chemical formula $C_{16}H_{32}$. Some isomers were present for both compounds.

2.1.2 Work-up procedure Ultidril, Novasol II and Petrofree

Wet sediment samples weighing 20-25 g were homogenized and placed in a Soxhlet tube. Internal standards, 1-dodecene and 1-eicocene (Ultidril), normal alkanes C_{16} and C_{22} (Novasol) 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 Ultidril tetra- and hexadecene content

The Ultidril liquid is a mixture of tetra- and hexadecene with small amounts of isomers. Quantitation was carried out by measuring the flame ionization detector response of the $C_{14}H_{28}$ and $C_{16}H_{32}$ area. The sum area was compared to the corresponding response of known amounts of the internal standards 1-dodecene and 1-eicocene.

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 4

Typical gas chromatograms are shown in Figure 3.1.

2.1.5 Determination of Novasol II alkane content

The Novasol II liquid is a mixture of eicosane isomers (SINTEF Report STF27 F94048, February 1995). 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 same conditions as for Ultidril (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, May 1994). 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 Ultidril (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 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

Ultidril
Two internal standards, 1-dodecene and 1-eicocene 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 Ultidril at 2000 ppm concentration level. An average recovery of 97% was obtained after work up and analysis of three replicate samples.

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.

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

Ultidril
The reproducibility of the analytical procedure was determined by analyses of sediment samples spiked with known amounts of Ultidril. From three replicate sediments samples spiked with Ultidril a relative standard deviation of 0,2% was obtained for the determination of the tetra- and hexadecenes.

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.

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.

Barium
The relative standard deviation for the determination of barium with x-ray is estimated to 5%. The repeatability of the x-ray measurement is 1-2%.

2.2.4 Quantitation limit

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

Novasol II
In these experiments the quantitation limit for Novasol II was set to 20 mg/ kg dry sediment.

Petrofree
In these experiments the quantitation limit for Petrofree ester was set to 5 mg/kg dry sediment.

3 RESULTS AND DISCUSSION

3.1 Ultidril

3.1.1 Content of Ultidril tetra-and hexadecene and barium in sediments from the Ultidril trays

The results from the analyses of the content of Ultidril tetra- and hexadecene and barium in sediment samples collected in the four Ultidril trays are given in Table 3.1 and Table 3.2. Table 3.1 gives the results of the content of Ultidril in the sediments. Table 3.2 gives the results of the barium content in the same sediment samples.

Figure 3.1 shows a gas chromatogram of a mixture of Ultidril spiked with 1-dodecene and 1-eicocene (internal standards) together with gas chromatograms of Ultidril sediments extracts (UBF 7) from day 3, day 62 and day 176.

A total of four trays were treated with Ultidril. In two trays, tray 5 and 8 Ultidril cuttings were used (UTD). In the other two trays, tray 2 and 7 Ultidril base fluid was used (UBF).

At intervals (day 3, 27, 62, 100, 160 and 176) samples were taken for Ultidril and barium analyses. The samples were collected at random. Each time one sample was taken from each of the four Ultidril trays.

The content of Ultidril tetra- and hexadecene and barium was analysed in the samples used in the Ultidril trays:

Ultidril cuttings:
The content of Ultidril was 97000 mg/kg dry cuttings.
The content of barium was 82000 mg/kg dry cuttings

Ultidril base fluid:
The content of Ultidril was 265000 mg/kg dry cuttings.
The content of barium was 1090 mg/kg dry cuttings

3.1.2 Discussion

In the present study the Ultidril mud liquid consists of tetra-and hexadecene. 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 results from the four Ultidril trays listed in Table 3.1 show that a pronounced reduction in the Ultidril content has taken place from day 3 to day 176. The concentration of the Ultidril tetra- and hexadecene is reduced more than 10 times in UTD 5 and UBF 2, and more than 20 times in UTD 8 and UBF 7.

Table 3.3 shows the ratio between the sum area tetradecene and the sum area hexadecene in the Ultidril samples. The ratio in the Ultidril standard mixture is the mean value of 15 measurements. The ratio in the sediment extracts is the mean value between all the analysed samples (4 trays from 6 samplings). The results clearly show that the reduction of tetradecene

has taken place faster than the reduction of hexadecene. This is also clearly illustrated in figure 3.1.

Barium and Ultidril 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 results from the analyses of barium are listed in Table 3.2. The main conclusion is that no reduction in the barium content in the two UTD trays (treated with Ultidril cuttings) has taken place. The variation in the barium content in these two trays is most probably due to inhomogeneity in the sample material.

Previous analyses of the control sediment (SINTEF report STF27 F94048, February 1995) gave a barium concentration of 810 mg/kg dry sediment (mean of three replicate samples). This means that no additional barium is detected in the two UBF trays (treated with Ultidril base fluid).

Table 3.1

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

Date		UTD 5	UTD 8	UBF 2	UBF 7
Day 3	94.11.18	773	1110	1150	888
Day 27	94.12.12	583	453	773	670
Day 62	95.01.16	315	509	733	344
Day 100	95.02.23	289	253	442	260
Day 160	95.04.25	198	74	103	81
Day 176	95.05.11	46	30	102	34

Table 3.2

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

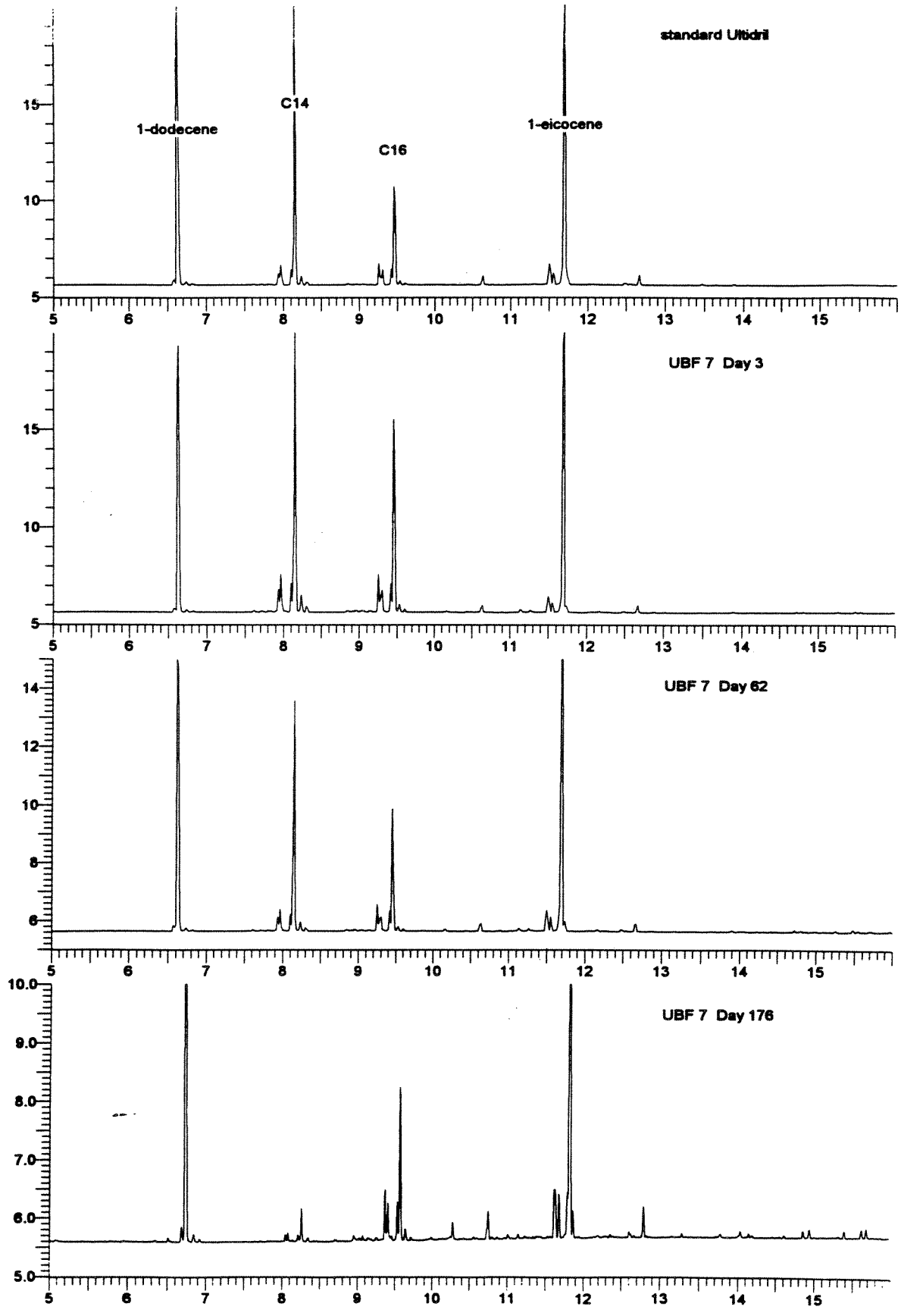
Date		UTD 5	UTD 8	UBF 2	UBF 7
Day 3	94.11.18	1630	2000	900	830
Day 27	94.12.12	1570	1590	880	820
Day 62	95.01.16	1490	1680	880	850
Day 100	95.02.23	1680	1540	850	840
Day 160	95.04.25	2120	1610	870	820
Day 176	95.05.11	1490	1230	870	830

Table 3.3

RATIO BETWEEN AREA OF TETRADECENE AND HEXADECENE IN ULTIDRIL
(sum area C_{14}/sum area C_{16}, mean values)

Date		Standard Ultidrill	Sediment extract of Ultidril
		1.8	
Day 3	94.11.18		1.8
Day 27	94.12.12		1.7
Day 62	95.01.16		1.6
Day 100	95.02.23		1.2
Day 160	95.04.25		0.87
Day 176	95.05.11		0.61

Figure 3.1
Gas chromatograms of Ultidril sediment extracts from day 3, day 62 and day 176 together with a standard of Ultidril tetra- and hexadecene. 1-dodecene and 1 eicocene are added as internal standards.



3.2 NOVASOL II AND PETROFREE ESTER

3.2.1. Content of Novasol II, Petrofree ester and Barium in sediments from the Novasol II and Petrofree trays.

The results from the analyses of the content of Novasol II eicosane isomers and Petrofree ester in sediment samples collected in their respective trays are given in Table 3.4. The content of barium in the sediment samples is given in Table 3.5.

Figure 3.2 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 3, day 62 and day 176.

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 3, day 62 and day 176.

At intervals (day 3, 27, 62, 100, 160 and 176) samples were taken for Novasol II, Petrofree and barium analyses. The samples were collected at random. Each time one sample was taken from the Novasol II and Petrofree tray repectively.

3.2.2 Discussion

The results from the Novasol II and Petrofree trays listed in Table 3.4 show a reduction in the Novasol II content from 570 mg /kg at day 3 to 200 mg/kg at day 176. The reduction of Petrofree ester is almost complete during the experiment period, from 803 mg/kg at day 3 to < 5 mg/kg at day 160 and day 176.

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

The results from the analyses of barium are listed in Table 3.5 The main conclusion is that no reduction in the barium content has taken place, either in the Novasol II tray nor in the Petrofree tray. The small variation in the barium content in these two trays is most probably due to inhomogeneity in the sample material.

3.3 Barium

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 3 to day 176. The minor variation in the content of barium in the sediment trays is most probably due to inhomogeneity in the sample material.

Table 3.4

CONTENT OF NOVASOL II EICOSANE ISOMERS AND PETROFREE ESTER IN SEDIMENTS
(mg/kg dry sediment)

Date		PAO 6 Novasol II	PTF 3 Petrofree
Day 3	94.11.18	570	803
Day 27	94.12.12	419	697
Day 62	95.01.16	336	435
Day 100	95.02.23	241	61
Day 160	95.04.25	242	< 5
Day 176	95.05.11	200	< 5

Table 3.5

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

Date		PAO 6 Novasol II	PTF 3 Petrofree
Day 3	94.11.18	1420	1450
Day 27	94.12.12	1290	1510
Day 62	95.01.16	1340	1550
Day 100	95.02.23	1370	1540
Day 160	95.04.25	1360	1450
Day 176	95.05.11	1220	1430

Figure 3.2
Gas chromatograms of Novasol sediment extracts from day 3, day 62 and day 176 together with a standard of Novasol II eicosane isomers. The alkanes n-$C_{16}H_{34}$ and n-$C_{22}H_{46}$ are added as internal standards.

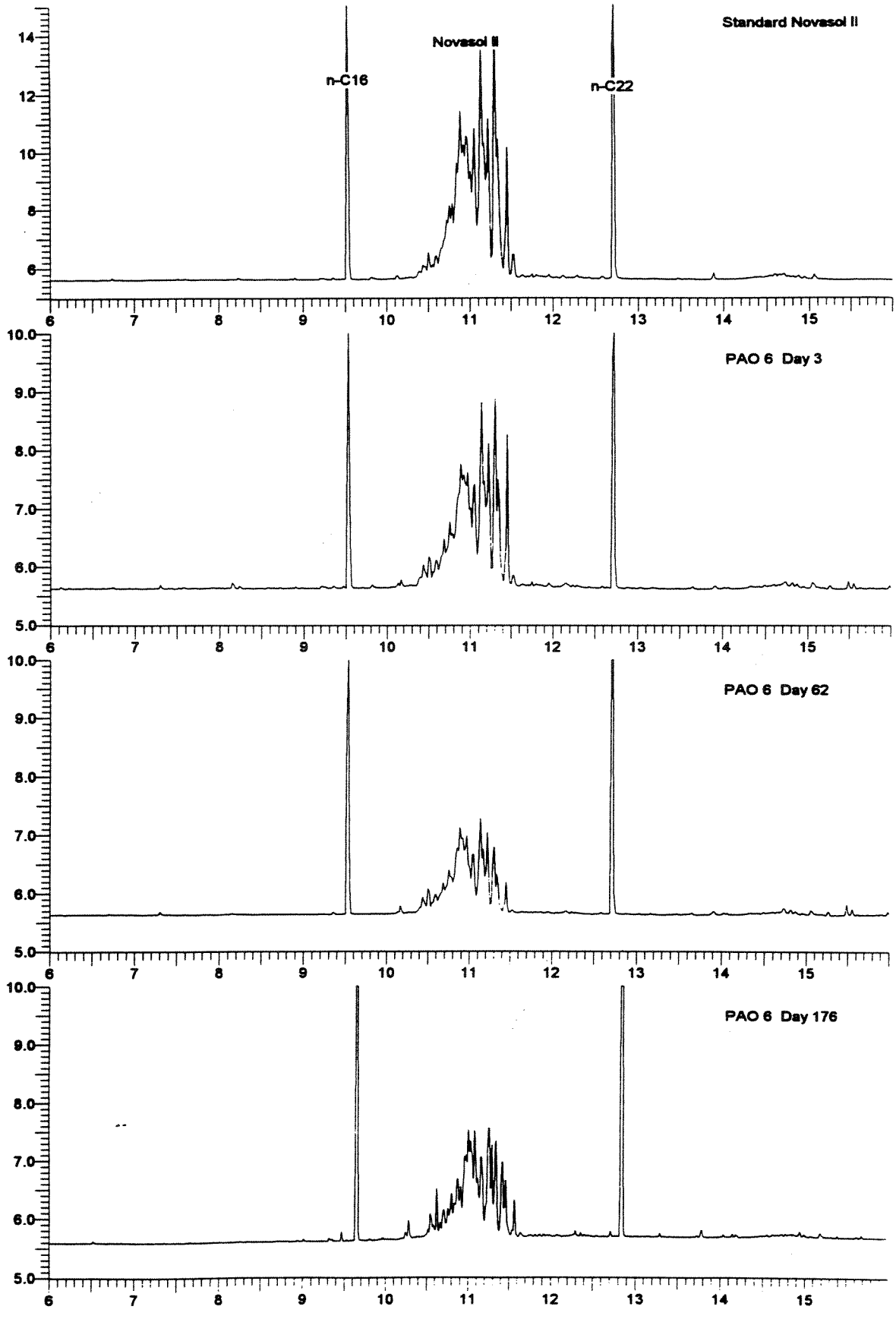
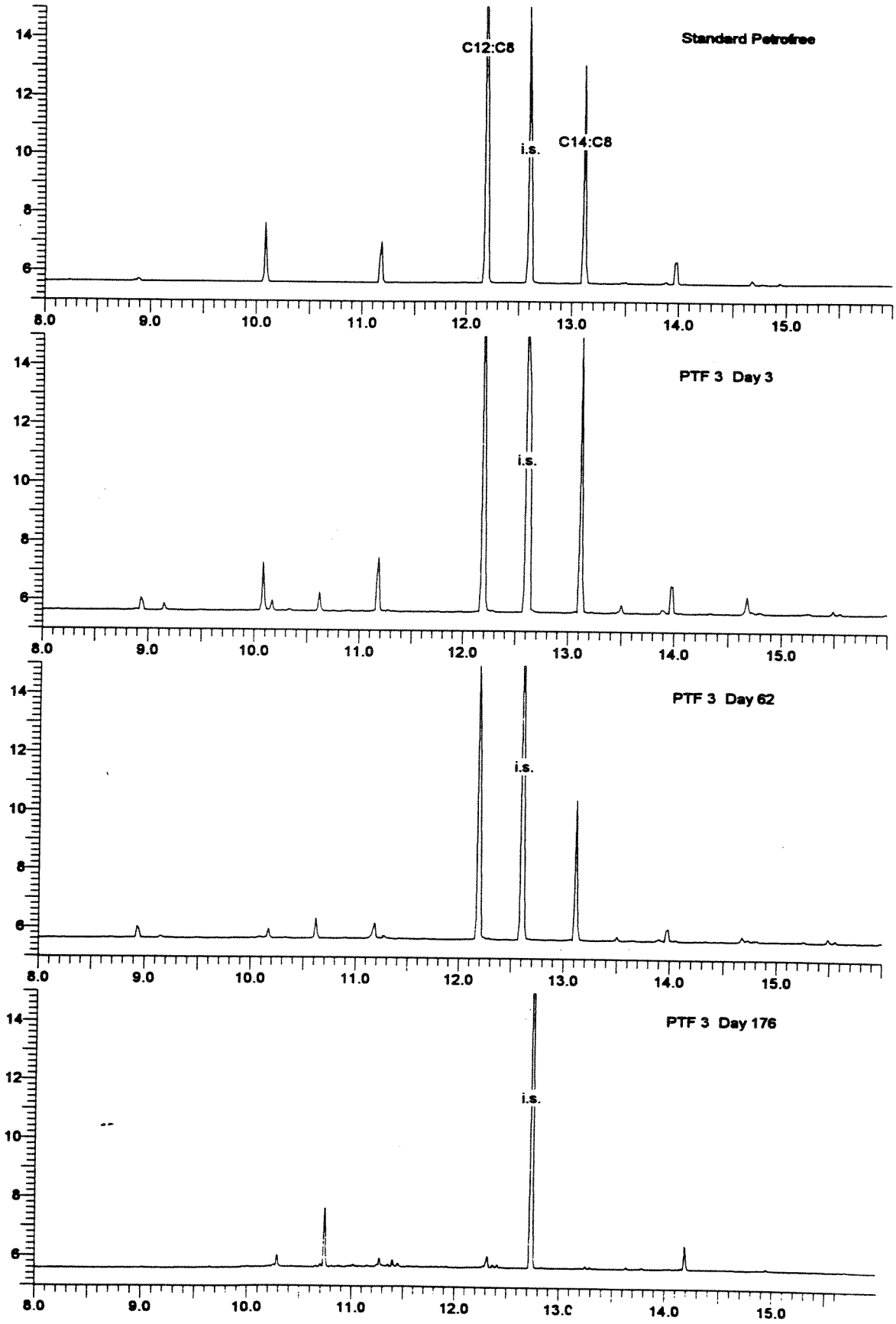


Figure 3.3
Gas chromatograms of Petrofree sediment extracts from day 3, day 62 and day 176 together with a standard of Petrofree ester. Ethyl stearate is added as internal standard.



Norwegian Institute for Water Research
P.O.Box 173, Kjelsås N-0411 Oslo, Norway
Phone: + 47 22 18 51 00 Fax: + 47 22 18 52 00

ISBN-82-577-2847-0