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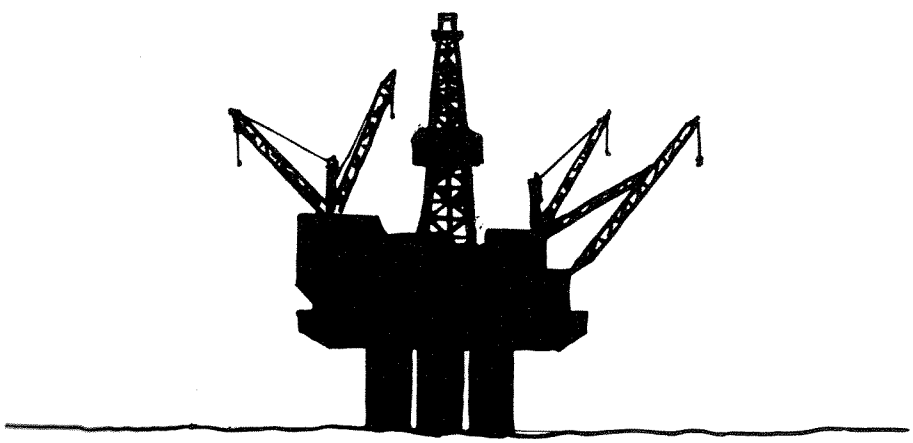
NIVAREPORT

Oil & Gas

O-90101

Tests on Degradation of a New Drill Mud Type under Natural Conditions

FINAL REPORT



NIVA – REPORT

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Report No.:

Sub-No.:

Serial No.: 2538

Limited distribution:

Report Title:

TESTS ON DEGRADATION OF A NEW DRILL MUD TYPE UNDER NATURAL CONDITIONS

Date: 30.01.1991

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Topic group: Oil and Gas

Geographical area: North Sea

Number of pages (incl. app.): 42

Contractor: BP Norway Limited U.A.

Contractors ref. (or NTNF-No): C-550125-1-A

Abstract:

Petrofree and Base Oil cuttings from offshore drilling were degradation tested in seminatural sea bottom ecosystems. Petrofree is a mixture of fatty acid esters. After 93 days the reduction in ester was significant and after 184 days close to 99%. Microbial degradation accounted for about 15%, while the rest probably was lost to the water as partly degraded metabolites. No significant loss was detected in the mineral oil cuttings, and biodegradation was less than 5%. Bacterial abundance increased at both treatments. Petrofree degradation was clearly slow compared to laboratory tests, but faster than the loss of the Base Oil.

4 keywords, Norwegian
1. Oljeboring
2. Kjemikalier
3. Nedbrytning
4. Sedimenter

4 keywords, English
1. Oildrilling
2. Chemicals
3. Degradation
4. Sediments

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For the Administration

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ISBN 82-577-1852-1

NORWEGIAN INSTITUTE FOR WATER RESEARCH

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FINAL REPORT

Oslo 30 January 1991

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PREFACE

This report describe the work conducted and results obtained under Contract no. C-550125-1-A with BP Norway Limited U.A., on the degradation testing of Petrofree and Base Oil drilling muds. Experiments were performed at NIVA Marine Research Station Solbergstrand (MRS), Norway, from June to December 1990.

The experiments were designed by NIVA in cooperation with BP and SI. Senter for Industriforskning (SI) was sub-contracted for chemical characterization of mud constituents and analysis of their fate in sediments. We want to express our gratitude to Frøydis Oreld, Jo Døhl and Nina Gjøs for excellent cooperation and performance. Their report is included as an Appendix.

Mesocosm experiments were established and sampling for chemistry was performed by Aud Helland and Roger Konieczny, and maintenance at MRS by Håkon Oen. Tone Jøran Oredalen sampled for microbiology and performed the respiration measurements. Åse Bakketun organized her and other assistants in the microbiology laboratory and plotted all results. It was a pleasure to note their enthusiasm and hard work.

In many respects we feel this work to be pioneering in terms of a systematic approach to the difficult task of degradation testing at environmentally realistic conditions. Without the professionalism and open mindedness shown by BP, and in particular John Addy, this would not have been the result. The test scheem developed here can be developed into a harmonized procedure for sediment fate and effects studies of offshore chemicals. We look forward to a continued cooperation in this area.

Oslo, 4. February 1991

Torgeir Bakke
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SUMMARY

An experiment was performed to test the degradation of two types of used mud on cuttings under conditions similar to those at the bottom around offshore platforms. One sample of cuttings contained a new drilling mud named Petrofree where the substitute for the base oil is a mixture of fatty acid esters. The other sample contained a standard low aromatic base oil mud. The cuttings were distributed on the sediment surface at two different concentrations (1000 and 10 000 ppm in the upper 1 cm) in 1 m^2 trays containing a seminatural sediment ecosystem. The trays were kept in darkness and immersed in flow through seawater.

Change in concentration of esters and total hydrocarbons respectively as well as total organic carbon, sediment respiration, bacterial abundance, and hydrolytic enzyme activity was followed for a period of 184 days.

The experiments showed that no significant degradation or other loss of the Petrofree esters occurred during the first 49 days. After 93 days the reduction in ester was detectable, but only statistically significant in the high dose tray due to patchiness in distribution of the cuttings on the sediment. During the same period of time no loss in total hydrocarbons was detected in the mineral oil cuttings. After 184 days the loss in ester was significant and in the highest dose close to 99 %, but lumps of cuttings still contained concentrations clearly above background. The loss of ester was not accompanied by any clearcut loss in total organic carbon from the sediment, probably due to high background concentration of sediment carbon.

The addititon of Petrofree resulted in an elevated and dose dependent sediment respiration indicating enhanced biodegradation activity. The results suggested that a significant fraction of the ester was lost to the water as partly degraded metabolites. The mineral oil had a slight temporary inhibitory effect on respiration at the high dose during the first 49 days.

Total bacterial abundance and hydrolytic enzyme activity reflected to some extent the addition of Petrofree, and showed that certain constituents were more easily degraded than others.

It must be concluded that the rate of degradation of Petrofree mud under natural conditions is distinctly slower than shown by a standardised OECD biodegradation test, but faster than the rate of loss of the generic base oil under the same conditions.

SAMMENDRAG

Det er gjennomført et eksperiment for å undersøke nedbrytningen av to typer kaks med boreslam under betingelser tilsvarende de som finnes på bunnen rundt installasjoner på sokkelen. Den ene kakstypen inneholdt en ny type boreslam ved navn Petrofree hvor oljen er erstattet med en blanding av fettsyre-estere. Den andre typen kaks inneholdt et standard mineraloljeslam. Kakset ble fordelt i to konsentrasjoner (1000 og 10 000 ppm i den øvre 1 cm) i 1 m^2 kasser med et tilnærmet naturlig bløtbunnssamfunn. Kassene ble holdt i mørke og neddykket i et større basseng med gjennomstrømmende sjøvann.

Forandringer i konsentrasjon av henholdsvis estere og total-hydrokarboner, totalmengde organisk karbon, sedimentrespirasjon, bakterietetthet, og aktivitet av hydrolytiske enzymer ble fulgt over en periode på 184 dager.

Forsøket viste at det ikke skjedde noe entydig nedbrytning eller annet tap av Petrofree ester i løpet av de første 49 dagene. Etter 93 dager var reduksjonen i mengde ester målbart, men bare statistisk entydig i kassen med høy dose. I samme tidsrom ble ikke konsentrasjonen av hydrokarboner endret i mineraloljekakset. Etter 184 dager var reduksjonen i ester entydig i begge doseringer, med tap på henimot 99% i den høyeste dosering. Reduksjonen i ester ble ikke ledsaget av noen entydig reduksjon i totalmengde organisk karbon grunnet relativt høyt naturlig organisk innhold i sedimentene.

Tilsats av Petrofree kaks førte til forhøyet og dose-avhengig sedimentrespirasjon, hvilket indikerer øket biologisk nedbrytning. Resultatene tyder på at en betydelig del av esteren forsvant gjennom utlekking av organiske nedbrytningsprodukter til vannet over. Mineraloljekakset hadde i høy dose svakt hemmende virkning på sedimentrespirasjonen i de første 49 dagene.

Bakterietetthet og enzymaktivitet reflekterte til en viss grad tilsatsen av Petrofree, og viste at visse komponenter i det tilsatte kakset var lettere nedbrytbare enn andre.

Det konkluderes at nedbrytningshastigheten av Petrofree slam under naturlige betingelser er klart langsommere enn det som er vist i en standardisert OECD-test, men raskere enn nedbrytningen av mineraloljeslam under samme forhold.

I N N H O L D S F O R T E G N E L S E

1. Introduction

On request from BP Norway Limited U.A. the Norwegian Institute for Water Research (NIVA) has investigated the rate and degree of biodegradation of a new type drilling mud. The work is covered by Contract no C-550125-1-A, and has been performed in cooperation with Senter for Industriforskning (SI).

The new type of drill mud has been produced by BAROID A/S. It is named "Petrofree Biodegradable Invert Emulsion Drilling Fluid". The substitute for the base oil in currently used muds is a mixture of fatty acid esters (major component 2-ethylhexyldodekanoate). Recent tests by standard biodegradability assays have described the organic content of the mud as 'readily degradable' (81% loss in 28 days at 20^0C, Baroid Corporation report 1990).

As a supplement to these investigations BP wished to obtain estimates on the degradability of Petrofree at realistic conditions. It was decided to perform such a test by use of soft bottom experimental ecosystems at low temperature (7-10^0C) and darkness. The degradation should be compared with simultaneous degradation of a typical base oil on currently produced cuttings under the same conditions. The experiment started in June 1990, with a test period of 184 days duration. The test was performed at the NIVA Marine Research Station Solbergstrand (MRS), Norway.

2. Methods

2.1 Experimental principle

The principle was to distribute realistic amounts of cuttings onto a natural marine sedimentary community and by various means measure the loss of Petrofree ester and and base oil as well as community response over time in darkness and at low temperature.

2.2 Experimental ecosystems

Five experimental sediment communities were applied for the test (cf. Berge et al. 1986 for a description of the communities). They were enclosed in fiberglass trays of 1 x 1 m sediment surface, and had an average sediment depth of 25 cm. The communities had been reared in

the MRS mesocosms since spring 1983, during which time recolonization and community stabilisation have proceeded. The communities hosted a vivid benthic fauna and a flora of natural microorganisms facultatively able to degrade the organic matter added.

The trays were immersed in a large basin with continuous low unidirectional current of water (approximately 1 cm/sec.) across the sediment surfaces. Nominal sea water exchange rate in the basin was 12 hrs. Water was pumped from 40 m depth in the fjord outside. During the experiment temperature ranged from 8^{0}C (June and November) to 12.7^{0}C (August and October) (Figure 1) and salinity from 31.4 to 34.2 o/oo. The system was generally kept at complete darkness or at low light intensity.

2.3 Test material

The following material was provided by BP for testing:

- 2 x 200 liters of Petrofree cuttings obtained from the Ross D rig (Manifest Reference R-012).

- 2 x 200 liters of unwashed mineral oil cuttings from the Ula D rig (Manifest Reference D-82/90).

- 2 x 200 liters of cleaned (i.e. washed) mineral oil cuttings from the Ula D rig (Manifest Reference D-82/90).

As reference for the testing of the Petrofree cuttings were selected the cleaned mineral oil cuttings. The test materials were designated 'Petrofree' and 'Washed' respectively.

2.4 Preparation

For each type of cuttings it was decided to apply two different doses of cuttings equivalent to 500 and 5000 mg/kg of total organics in the upper 1 cm of the sediment (Table 1). Hence, five trays were applied, two dosed with Petrofree, two with Washed and one clean Control. Above each of the trays a water column of about 1 m height was sealed off by plastic sheet walls. The weighed portion of cuttings was shaken with sea water for 2x1 minutes and the suspensions of fine material added to the surface of the enclosed water column and allowed to settle

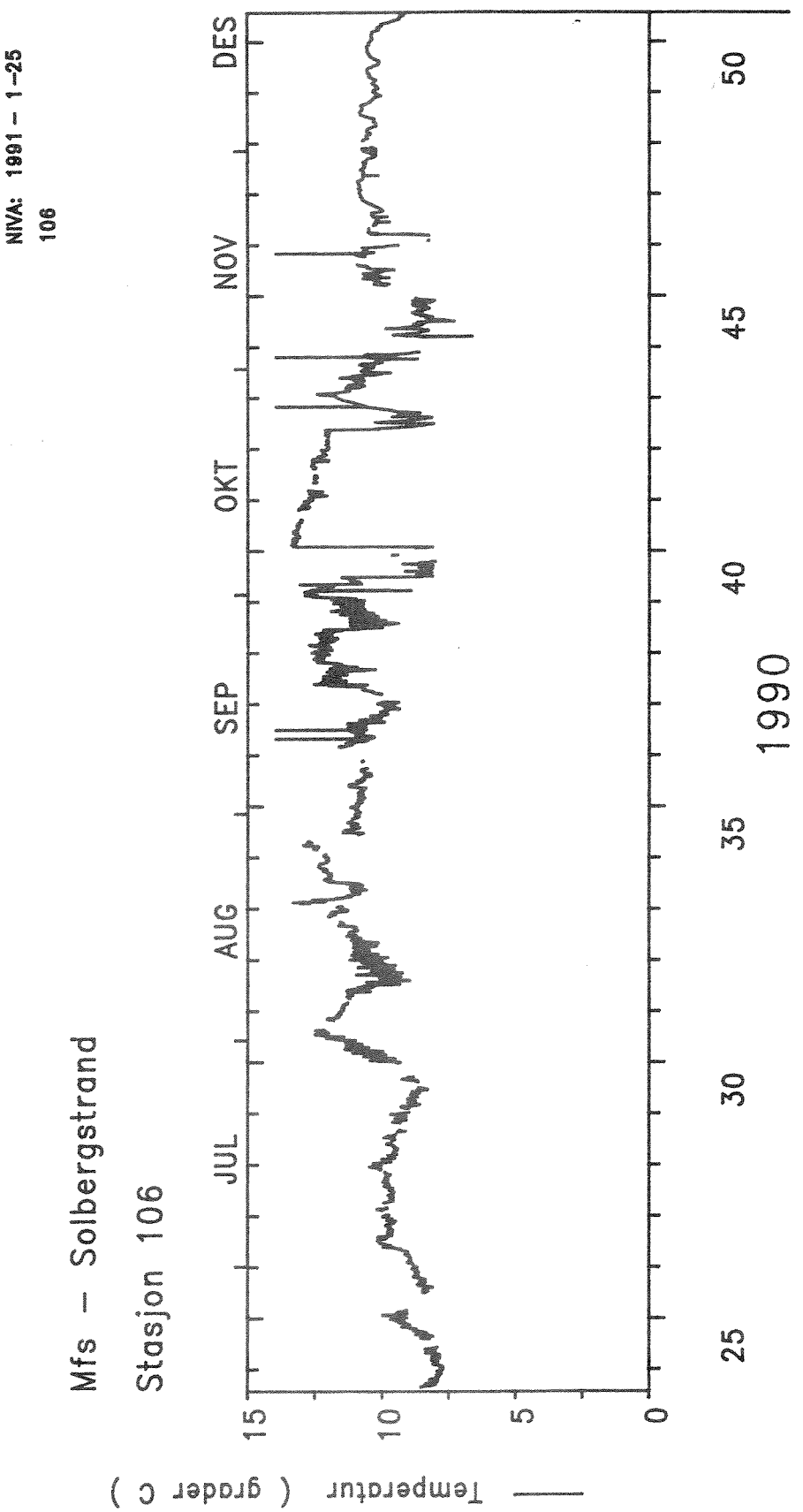

Figure 1. Water temperature fluctuation during the experiment. Hourly recordings plotted.

through the water onto the sediment. The coarse material was then distributed as randomly as possible onto the sediment surface.

The procedure aimed at preparing a contamination pattern similar to what is found around platforms, with a patchy distribution of the coarser cuttings and a more evenly distribution of the fine material. The provided Petrofree cuttings were considerably coarser than the Washed making the Petrofree test surfaces most patchy.

The plastic sheet walls were kept mounted for 72 hours until no visible turbidity could be seen in the enclosed water columns. After that the sheets were removed and the water level of the basin lowered for standard water movement across the sediments. The trays had been arranged in a row perpendicular to the current direction to avoid cross contamination.

Table 1 Overview of test sediments and their preparation.

Tray id.	Exposure type	Amount of cuttings added (g/tray)	Estimated amount of organics added (mg/kg dry sediment)[1]) organics:	carbon: [2])
P-500	Petrofree low	51.9	1 000 (ester)	770
P-5000	Petrofree high	519.0	10 000 (ester)	7700
W-500	Washed low	123.1	1 000 (MOM)	850
W-5000	Washed high	1231.0	10 000 (MOM)	8500
C	Clean control	0.0	0	0

[1])on basis of an assumed 60% water content of the tray sediments.

[2]) molpercent carbon in Petrofree estimated to 77 % (factor 1.3)
molpercent carbon in Washed estimated to 85 % (factor 1.17)

2.5 Sampling and measurements

The sampling timetable for the various purposes is given in Table 2. Sediment samples for chemical analysis were taken by use of hand-held corers (45 mm diam.) to a depth of 15 cm. To prevent exessive disturbance to the surrounding sediment a slightly wider corer was pushed into the sediment outside the main corer and left in place as the core sample was withdrawn. For analytical purposes the upper 1 cm

of each core was secured and frozen.

Table 2. Timetable of experimental setup, sampling and measurements

Activity or parameter	Date of activity								
	18-20/6	21/6	27/6	2/7	9/7	16/7	6/8	29/8	19/9	19/12
Preparation	X									
Petrofree ester		X	X	X	X	X	X		X	X
Washed THC		X	X	X	X	X	X		X	
Organic carbon		X	X	X	X	X	X	X	X	X
Esterase activity		X	X	X	X	X	X	X	X	X
Sediment respiration		X	X	X	X	X	X	X	X	X
Bacterial abundance		X	X	X	X	X	X	X	X	X
Day no.		2	9	14	21	28	49	71	93	184

Independent cores for microbiological analysis were taken in a similar manner (20 mm core diam.) to the same depth and kept at ambient temperature until analysis within 24 hours. The upper 2 cm of each core was sliced off and hogenized by gentle stirring before subsampling.

In general core samples were taken in triplicate from three separate quadrants of the tray. The sampling position within the quadrant was determined at random. At the two last sampling occations for Petrofree ester two of the three parallell cores were taken to cover visible lumps of cuttings, the third was taken outside such lumps.

Sediment respiration was estimated from direct measurement of decrease in oxygen concentration of the water inside an acrylic bell jar pushed into the sediment. The bell jar enclosed a sediment area of 95.0 cm^2, and was equipped with an YSI oxygen probe and a magnetic stirring device for gentle water circulation. Measurement was performed over a period of 2 hours and at the same sediment area each time, except for day 49, 93, and 184 when new sediment areas were enclosed and the measurement performed over a period of 24 hours.

2.6 Analytical procedures

Total hydrocarbons and Petrofree ester

Methods of analysis are detailed in the report from SI (Appendix 1). The analysis of total hydrocarbons (THC) was performed on samples from the Washed and Control trays, analysis of ester from the Petrofree and Control trays.

Total organic carbon (TOC)

TOC was analysed at NIVA on subsamples from the cores used for microbiological analysis. From the homogenate about 1 g wet weight was subsampled, freeze-dried and grinded in a mortar. After treatment with HCl vapours over night in a dessicator to remove inorganic carbon, triplicate samples were dried at 80^{0}C, 5-10 mg weighed into Sn capsules and analysed on a Carlo Erba Mod. 1106 Element Analyzer.

Of the remaining homogenate 5.0 g was diluted 1:10 with sterile seawater (45 g), mixed on Whirlmixer for 5 min. and kept at 15^{0}C. Coarse particles were removed by decanting after 45 min. sedimentation and aliquots of 5.0 ml used for bacterial abundance, MPN of oil degraders, hydrolytic enzyme activity, and dry weight measurements.

Hydrolytic enzyme activity

Total microbial activity in soil, sediments and water can indirectly be monitored as activity of hydrolytic enzymes capable of cleaving the fluorescent substrate 3',6'-diacetyl-fluorescein (FDA) (Schnurer and Rosswall 1982). A number of different enzymes present in bacteria can catalyze the reaction. Each sample was amended with 20 µl FDA solution (2 mg/l in acetone), background activity read at time 0 hours by fluorescence spectrometry (exitation 490 nm, emmission 510 nm) and the samples incubated at 15 ^{0}C for 3 hours until measured again.

Bacterial abundance

Bacterial abundance in upper 2 cm of sediment was monitored as colony-forming units (CFU) on triplicate spread-plates of a low nutrient seawater medium (0.1 % trypton, glycerol and yeast extract with 1.5 % agar in aged seawater). The results are given as arithmetic means. Attempts were made to monitor specific counts of hydrocarbon degraders

by MPN dilutions with diesel oil as carbon source, according to a standardized method. This method failed presumably due to high toxicity of the diesel oil.

3. Results and discussion

3.1 Total hydrocarbons (THC) and ester

The results are outlined in Table 3 and presented and discussed in detail in Appendix 1. The project necessitated development of a proper analytical procedure for the Petrofree ester. The procedure (described in Appendix 1) included continual extraction by both a polar and unpolar solvent which should secure both the esters and their potential splitting into alcohol and fatty acids. It proved to work very well.

The results showed that there were some loss of Petrofree esters from the sediments within 93 days of deposition, and a clear loss by day 184.

In the P 500 tray the initial concentration varied from 14 to 2720 mg/kg among replicate cores, reflecting the considerable patchiness in distribution of cuttings on the sediment. The day 9-21 results from pooled samples would alone indicate a significant and rapid loss of ester, but the day 28 pooled level of 616 mg/kg, being only slightly lower than the initial mean of 930 mg/kg, shows that at least some spots in the sediment had considerable amounts of ester left. Hence, one cannot conclude with confidence that a significant reduction in ester had occurred up to day 28.

After 93 days lumps of cuttings were still visible. Two such areas were sampled and gave <5 and 180 mg/kg respectively. In comparison with the highest level found at day 2, presumably also reflecting lumps of cuttings, one must conclude that the loss of ester had been significant within day 93. The same sampling strategy was applied after 184 days. The results show that the ester concentration was at background in the sediment area having no visible signs of cuttings, whereas the samples containing lumps of cuttings showed ester concentrations of 45 and 63 mg/kg.

In the P5000 tray the day 2 concentrations ranged from 2340 to 9560 mg/kg with a mean of 5810 mg/kg. The mean levels at day 9 to 49 varied between 1530 and 11100 mg/kg with no trend of decrease. After 93 days the two cores taken from areas with visible cuttings contained less

Table 3. Concentrations of Petrofree ester and total hydrocarbons in the upper 1 cm of sediment samples from the test trays (mg/kg dry sediment)

Petrofree cuttings (mg ester / kg dry sediment):

Treatment	Date							
	21/6 Day2	27/6 Day9	2/7 Day14	9/7 Day21	16/7 Day28	6/8 Day49	19/9 Day93	19/12 Day184
P 500 1	58						< 5	< 5
P 500 2	14	13	< 5[1]	< 5[1]	616	-[2]	180	62.5
P 500 3	2720						< 5	45.2
P 5000 1	9560						587	< 5
P 5000 2	5530	10060	3230	1530	11100	2360	896	50.3
P 5000 3	2340						21	97.2
K1	< 5						< 5	*
K2	< 5	*	*	*	*	*	< 5	*
K3	< 5						*	*

Washed mineral oil cuttings (mg THC / kg dry sediment):

Treatment	Date						
	21/6 Day2	27/6 Day9	2/7 Day14	9/7 Day21	16/7 Day28	6/8 Day49	19/9 Day93
W 500 1	103						409
W 500 2	156	155	167	91	148	372	310
W 500 3	79						32
W 5000 1	1710						7260
W 5000 2	3560	1940	2740	3270	3450	6320	897
W 5000 3	6750						1320
K1	28						28
K2	36	*	*	*	*	*	*
K3	26						*

* sampled, but not analysed

[1] <5: below detection limit for the ester.

[2] Sample lost during preparation.

than 900 mg/kg and the one from a 'clean' area as low as 21 mg/kg. It is therefore obvious that a significant loss of Perofree ester occurred between day 49 and 93. During that time there was also a visible loss of integrity of the lumps of cuttings on the surface. At day 184 a further loss of ester was recorded. The sample taken from a 'clean' area was at background concentration, and the two containing cuttings had ester concentrations of 50 and 97 mg/kg.

One must therefore conclude that the ester analysis showed no convincing loss of Petrofree ester during 1.5 month of exposure to the natural environment, and that a significant, although not complete, loss of Petrofree ester occurred during 6 months. Figure 2 shows the change in ester concentration with time in the P5000 tray. The use of average concentrations is not entirely justified since the samples at day 93 and 184 were not taken at random, but still the figure suggests that the loss of ester followed a roughly logarithmic pattern.

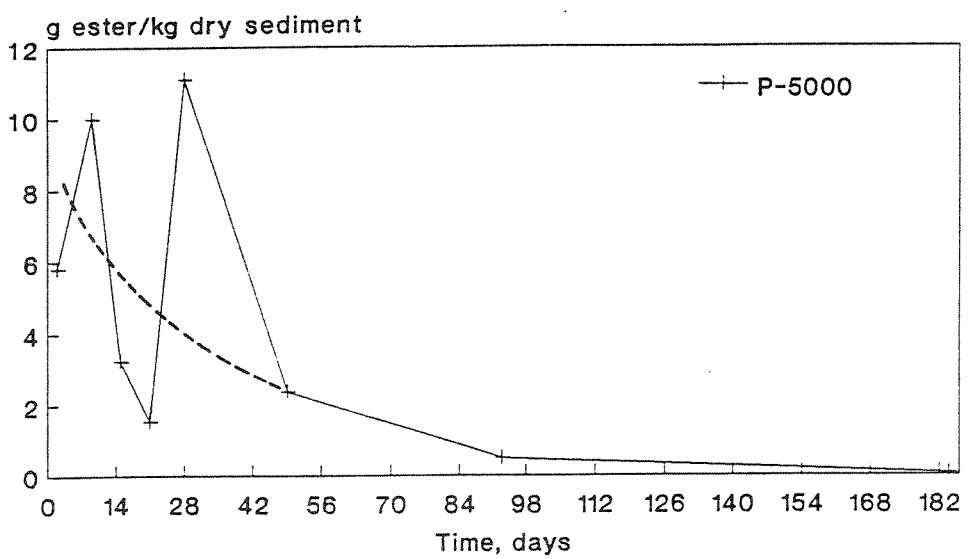

Figure 2. Change in mean concentration of Petrofree ester with time in the upper 1 cm of the high dose tray.

Table 3 also shows that the remaining content of ester on lumps of cuttings was essentially the same in the high and low dose tray after 184 days, i.e. that the loss of ester from individual lumps of cuttings was independent of the total amount of cuttings added.

The variation in total hydrocarbons among replicate cores at day 2 in the Washed trays was considerably less than the ester variation in the Petrofree trays, reflecting a more homogenous distribution of cuttings

in the former (Table 3). This was also observed during the addition of the cuttings. The change in THC concentration with time showed no significant loss of base oil within 93 days neither in the W500 nor the W5000 tray. These findings are in accordance with the general experience of low degradability of base oil around offshore drilling sites. No analysis were performed on the Washed trays after 184 days, but samples from day 220 (7.5 months) will be processed and reported separately.

3.2 Total organic carbon (TOC)

In the Washed trays there was no change in TOC, except for a fluctuation comparable to the control (Figure 3). The additions made up 24-30 % of the TOC at the high doses and 2-4 % at the low doses. The Petrofree trays showed an initial strong fluctuation and some reduction in TOC with time. This loss may not reflect degradation of the Petrofree ester, since the loss was much higher than could be expected from the amount of ester addedat the low dose. There was no good dose related response as the P-500 sediment showed about the same or even higher loss than the P-5000. There is reason to suspect that the Petrofree cuttings contained other unevenly distributed organic material. In particular fibers of cellulose were observed by microscopic examination of the dried and ground-up samples used for TOC. If so, such material may have disappeared (resuspension or dissolution) when the cuttings gradually disintegrated.

The level of organic carbon was slightly different in the 5 trays before any additions were made. These artefacts are not believed to have influenced other measurements, except perhaps for the background respiration.

3.3 Respiration

The change in sediment oxygen consumption is shown in Figure 4. A trend of persistent elevated respiration in the P-5000 sediment was evident for the whole period, indicating continuous degradation of the added substances. For Petrofree there was a clear dose-dependent relationship, with total oxygen consumption in P-5000 being about 4 times higher than in P-500 when control tray values are subtracted (Figure 5). After 184 days the respiration in the low dose sediments was the same as in the Control.

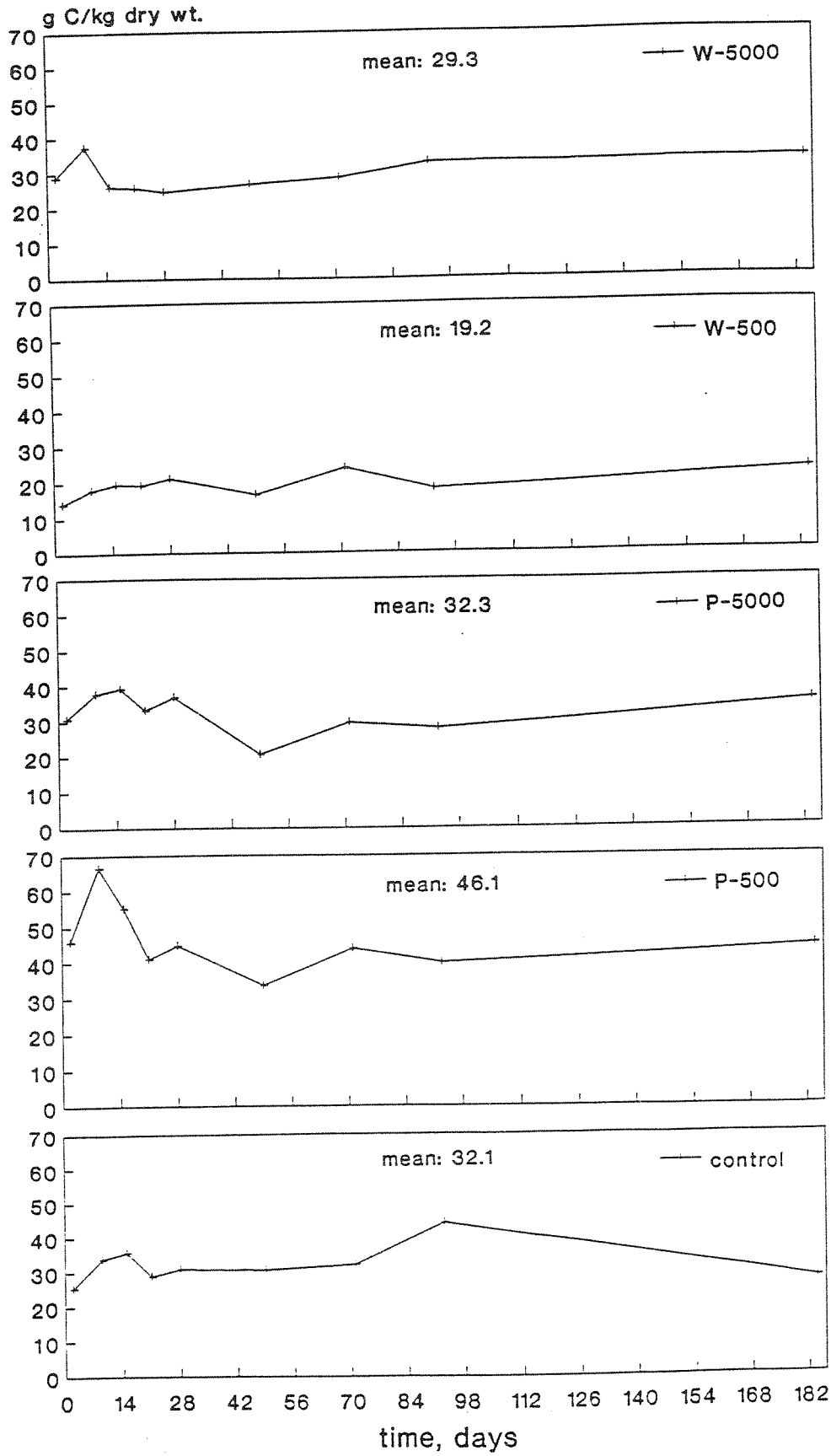

Figure 3. Change in total organic carbon (TOC) with time. Arthmetic mean of 3 samples.

Also the Washed trays showed higher total oxygen consumption than the control sediment over the 184 day period (Figure 5), but here only a weak dose-related response was found. This may be due to initial inhibitory effects of the high dose of base oil on community respiration (Figure 4). The high dose tray showed an elevated respiration in the last part of the test period, indicating reduced toxicity or improved availability for degradation of the hydrocarbons.

Community respiration relative to control for the 184 day period is the most direct way of measuring the contribution from biodegradation in the removal of the added chemicals. When converted to carbon removal the figures can be compared with the TOC added, as calculated in Table 1. The results are given in Table 4. They show that for Petrofree the microbial mineralization may account for 15-20 % loss of the added chemicals, depending on dose. Corresponding figures for Washed were 4.5-39 %. However since the background respiration may have varied among the boxes (not possible to state), we consider only the high dose estimates to be reliable, namely 15 % for Petrofree and 4.5% for Washed.

Table 4. Conversion of cumulative net community oxygen consumption to organic matter completely degraded during 184 days.

Treatment:	P-500	P-5000	W-500	W-5000
Net respiration (g O_2/m^2)	6.98	51.4	14.8	17.1
Carbon converted to CO_2 (µg C/mg dw.) [1]	0.16	1.15	0.33	0.38
Mean TOC in sediment (µg/mg dw.) [1]	46.1	32.3	19.2	29.3
Respiration loss in % of the mean TOC in sediment [1]	0.34	3.6	1.7	1.3
TOC added with cuttings (mg/kg dw) [2]	770	7700	850	8500
Respiration loss in % of the TOC added as chemicals [2]	(20)	15	(39)	4.5

[1]) in the upper 2 cm of the sediment
[2]) in the upper 1 cm of the sediment

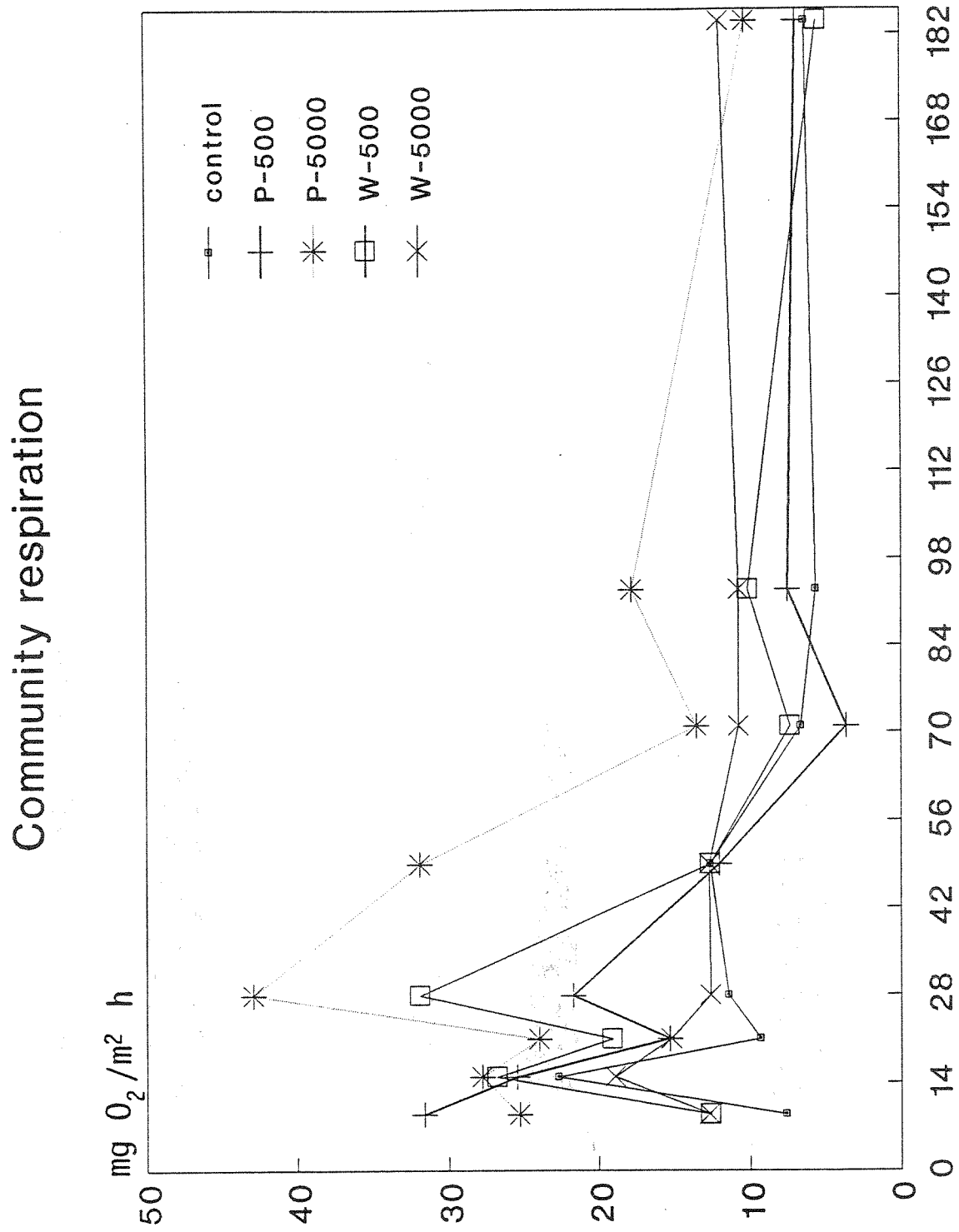

Figure 4. Change in community respiration with time in all trays.

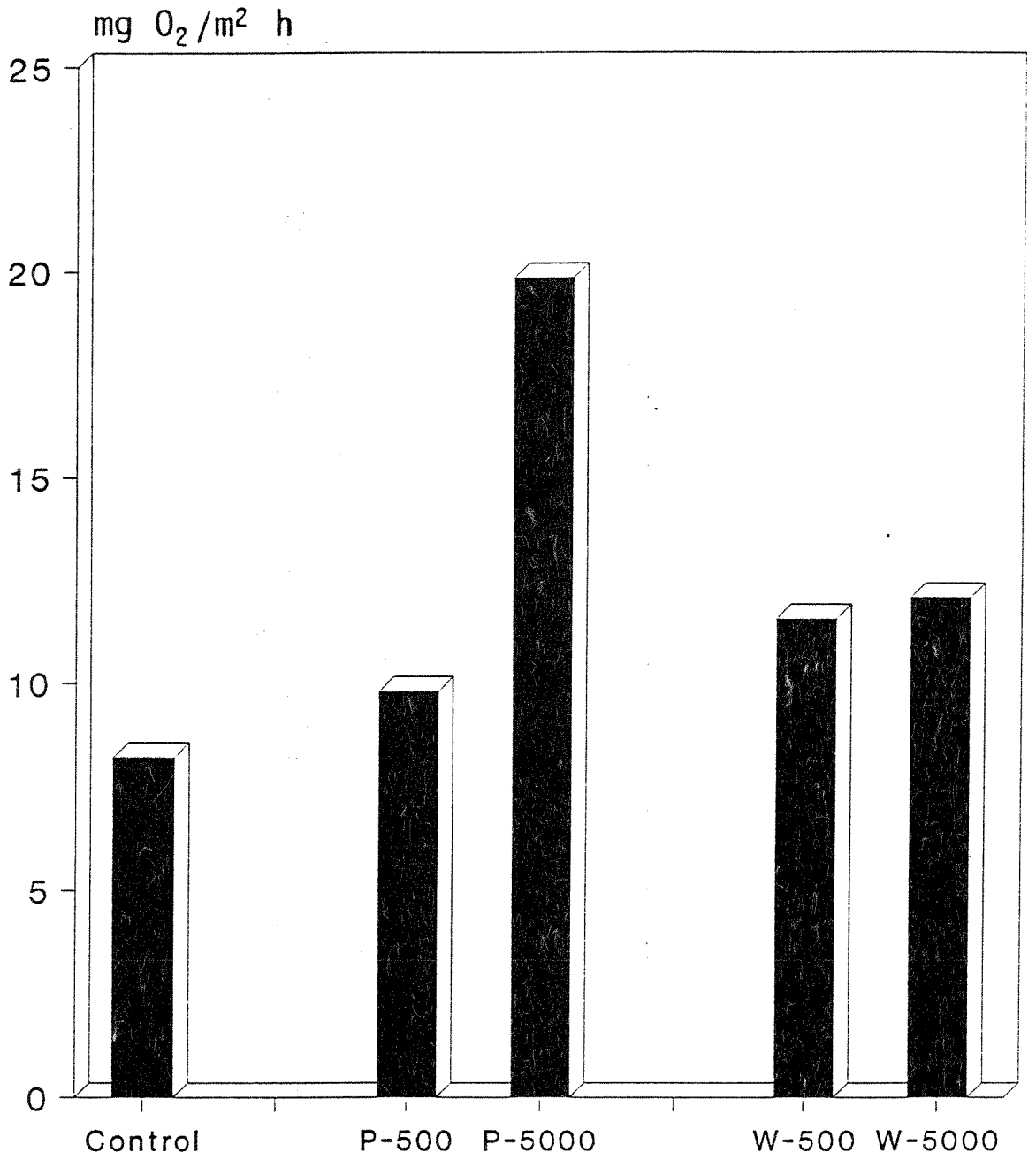

Figure 5. Average community respiration integrated over 184 days.

The calculation implies that respiration accounts for about 15 % loss of ester from the P-5000 tray during the 184 day period. In spite of a considerable scatter of figures, the total loss of ester shown in Table 3 and Fig.2 was much higher than this (around 90-99 %). The most probable explanation is that biodegradation has not gone all the way to CO_2 and water, but to intermediate products such as fatty acids. Since such products were not detected in the chemical analysis, even though the procedure was appropriate, they most probably have disappeared by dissolution to the overlying water prior to further breakdown. For the Washed cuttings, however, the low estimate of 4.5 % respiration based loss in the high dose is in good accordance with the chemical data.

3.4 Bacterial abundance

Total bacterial abundance showed a clear dose dependent response to Petrofree in consistence with the respiration results (Figure 6), while the Control abundances were low and stable. However, a 3-phase development after a lag period of up to 9 days indicated that some inhibitory substances may have been present, and that certain fractions of the organic material were degraded before others. These data are also consistent with the results on respiration.

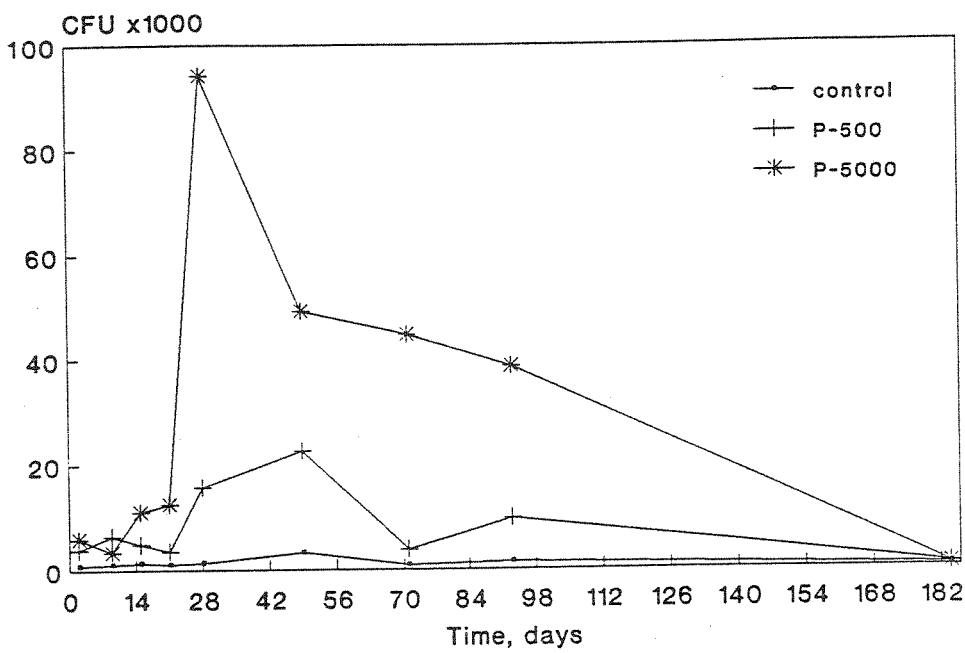

Figure 6. Bacterial abundance in the top 2 cm of the sediment. Petrofree and Control trays.

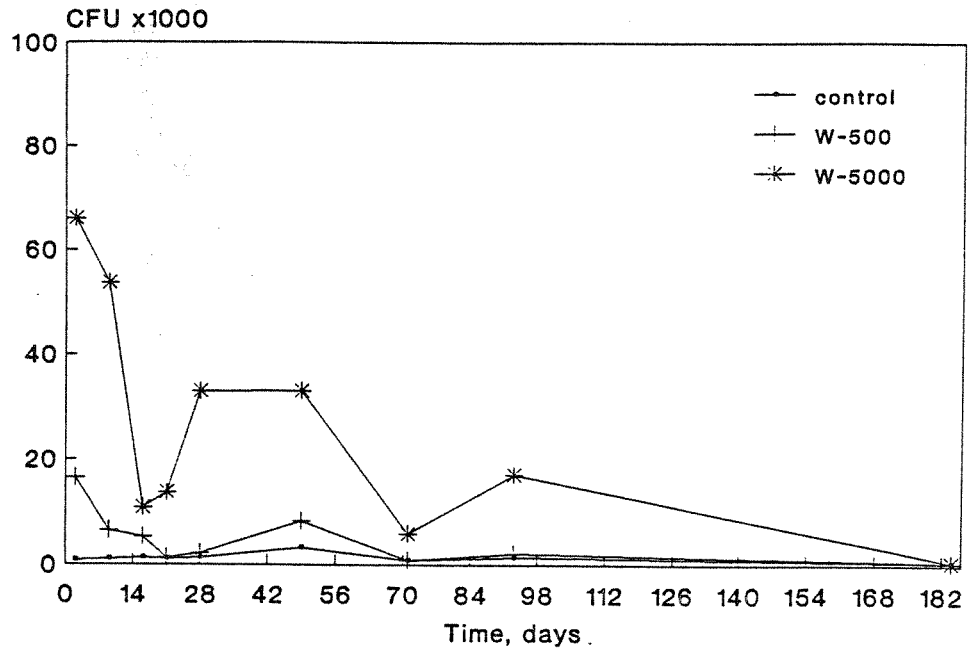

Figure 7. Bacterial abundance in the top 2 cm of the sediment. Washed Mineral Oil and Control trays.

For the Washed trays very high initial counts were observed that must be due to bacteria present in the mud at start (Figure 7). These disappeared during the first 2 weeks, and then a new population developed, showing a dose-related response. These data are, however, not consistent with respiration which was initially highest at the low dose. For both treatments bacterial abundances were at control levels after 184 days.

3.5 Hydrolytic enzyme activity

Hydrolytic enzyme activity increased rapidly in the P-500 tray in consistence with the 3-phase development in bacterial abundance, while the high dosage P-5000 was equivalent to control (Figure 8). Induction of elevated enzyme activity is in general indicative of limitation in degradable substrate. The high enzyme levels in P-500 thus probably reflected that biodegradation was substrate-limited in this tray, while other factors (i.e. nutrients, oxygen availability, toxicity) may have been limiting in the P-5000 tray.

The mineral oil trays showed a sharp peak as the initially high bacterial counts declined, which also indicate that this population

became substrate limited (Figure 9). A later increase is also consistent with substrate limitation, with a higher level at the low dosage.

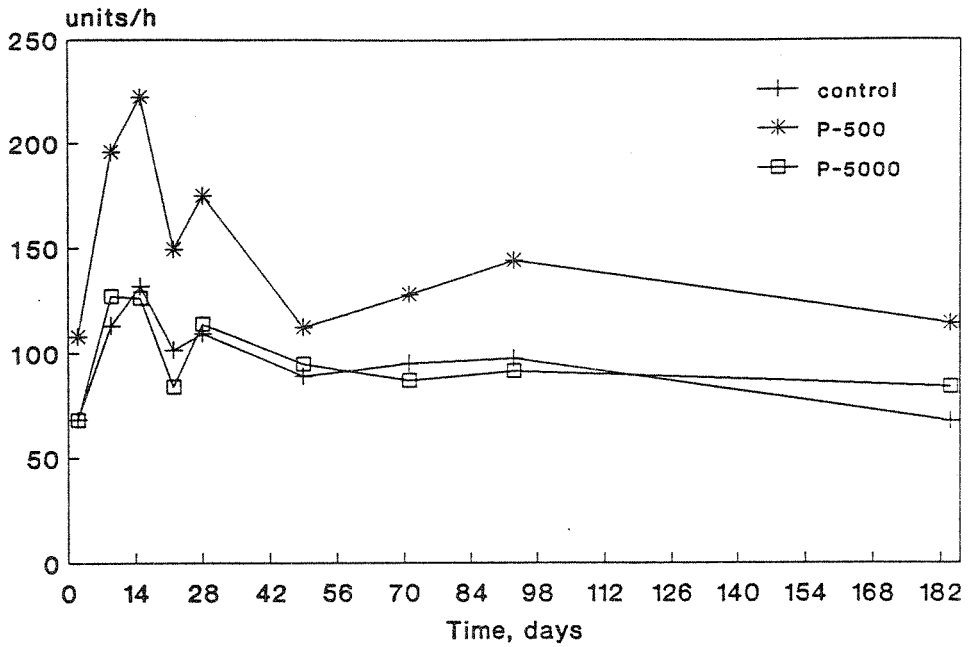

Figure 8. Hydrolytic enzyme activity in the upper 2 cm of the sediment. Petrofree and Control trays.

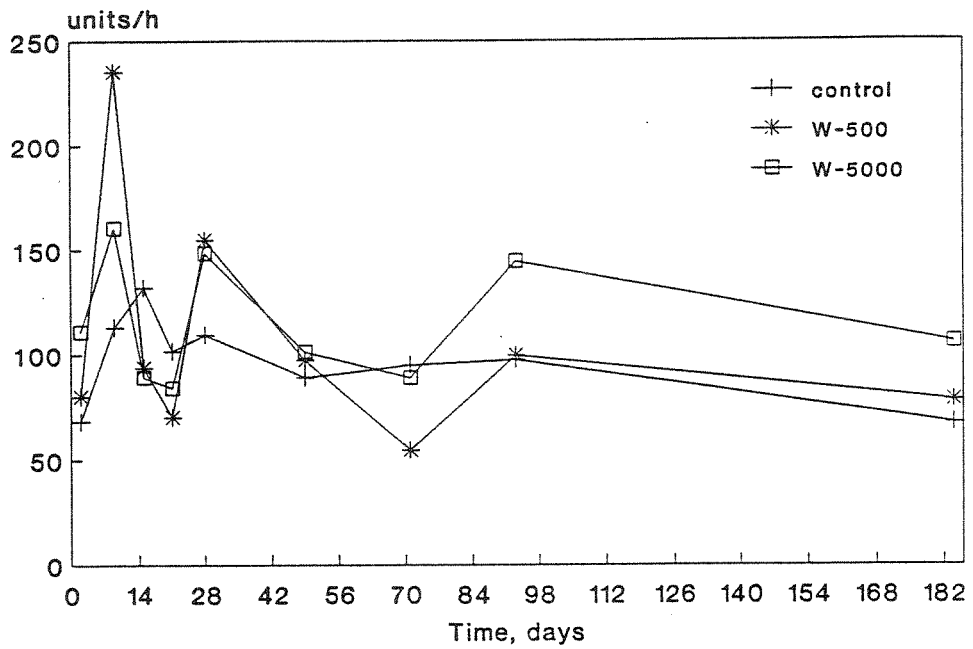

Figure 9. Hydrolytic enzyme activity in the upper 2 cm of the sediment. Washed Mineral Oil and Control trays.

The results confirm that both types of cuttings contained biodegradable fractions which would stimulate hydrolytic enzyme activities in times of substrate limitation. However, since the specific (per CFU) enzyme level in the control was higher than the others, probably due to extreme substrate limitation, direct comparisons are difficult. A quantitative relationship with degradation is not to be expected for hydrolytic enzymatic activity.

4. General conclusions

The experiments showed that no significant degradation or other loss of Petrofree ester occurred during the first 49 days after the cuttings had been disposed onto the experimental sea bottom. After 93 the reduction in ester was detectable, but only statistically significant in the high dose tray due to patchiness in distribution of the cuttings on the sediment. During the same period of time no loss in total hydrocarbons was detected in the washed mineral oil cuttings. After 184 days the loss in ester was significant and in the high dose close to 99 %, but lumps of cuttings still contained concentrations clearly above background. The loss of ester was not accompanied by any clearcut loss in total organic carbon from the sediment, probably due to high background concentration of sediment carbon.

The loss in Petrofree ester was also reflected in elevated and dose dependent sediment respiration indicating biodegradation of organic matter. Comparison of oxygen consumption with loss in ester suggested that a significant fraction of the ester had been lost as metabolites leaking to the overlying water rather than by complete mineralization to CO_2 and water at the sediment.

The successive change in total bacterial abundance and in hydrolytic enzyme activity reflected to some extent the addition of Petrofree, and showed that certain constituents of the organic matter added were degraded before others. The results also showed that the washed mineral oil cuttings contained a considerable bacterial population when added to the sediments, and that this population gradually yielded to other populations with time.

It must be concluded that the rate of degradation of Petrofree mud under natural conditions is far slower than shown by standardised biodegradation tests, but faster than the rate of loss of a generic base oil under the same conditions.

5. References

Berge, J.A., Schaanning, M., Bakke, T., Sandøy, K.A., Skeie, G.M., and Ambrose, W.G., 1986. A soft bottom sublittoral mesocosm by the Oslofjord: description, performance and examples of application. Ophelia 26, 37-54.

Schnurer, J., and Rosswall, T., 1982. Fluorescein diacetate hydrolysis as a measure of total microbial activity in soil and litter. Appl. Environ. Microbiol. 43, 1256-1261.

APPENDIX

TESTS ON DEGRADATION OF A NEW DRILL MUD TYPE UNDER NATURAL CONDITIONS - CHEMICAL ANALYSIS

SI-report no 900914

TESTS ON DEGRADATION OF A NEW DRILL MUD TYPE UNDER NATURAL CONDITIONS - CHEMICAL ANALYSIS

by

Frøydis Oreld, Jo Døhl and Nina Gjøs

SI-report 900914

1991

REPORT No : 90 09 14

This report : CONFIDENTIAL
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TESTS ON DEGRADATION OF A NEW DRILL MUD TYPE UNDER NATURAL CONDITIONS - CHEMICAL ANALYSIS

by Frøydis Oreld, Jo Døhl, Nina Gjøs

PROJECT : Contract no. O-90101

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4 index words:

Norwegian	English
Boreslam	Drilling mud
Nedbrytning	Degradation
Hydrokarboner	Hydrocarbons
Fettsyreestere	Fatty acid esters

Number of pages: 20

TABLE OF CONTENTS

1. INTRODUCTION

On request from BP Norway Limited U.A. the Norwegian Institute for Water Research (NIVA) is investigating the rate and degree of biodegradation of a new type drilling mud.

The new type of drilling mud has been produced by BAROID A/S. The substitute for the base oil in currently used muds is a mixture of fatty acid esters, claimed by the producer to be completely degradable. This is at present being tested by standard biodegradation assays.

As a supplement to these investigations BP wishes to get rapid results on the degradability from tests performed in soft bottom experimental eco-systems at low temperature (7-10^{0}C) and darkness. The degradation should be compared with simultaneous degradation of a generic base oil on currently produced cuttings under the same conditions. On request from NIVA, Center for Industrial Research (SI) has performed the chemical analysis in this project.

The present report presents the methods and results of the chemical analyses of both the new Petrofree mud and mineral oil mud.

Project manager at SI : Frøydis Oreld

Participants at SI : Jo Døhl
Nina Gjøs
Anne Norsted
Tone Øfsti

2. MINERAL OIL MUD

DESCRIPTION OF THE ANALYTICAL PROCEDURES AND QUALITY ASSURANCE PROGRAMME FOR THE CHEMICAL ANALYSIS

2.1. ANALYTICAL PROCEDURES

2.1.1. Work up procedure - hydrocarbons

The chemical analysis includes the determination of total hydrocarbon content (THC). A detailed account of the quality assurance programme for the chemical analysis is given in section 2.2. below.

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

Wet sediment samples weighing approximately 20 g were homogenized. The samples were thereafter saponified in 80 ml of 0.5 M methanolic KOH under reflux for 2 hours.

The mixture was filtered under suction and washed with 50 ml methanol and finally extracted twice with dichloromethane (DCM). The combined DCM extracts were washed with water and dried over Na_2SO_4. The sediment extracts were then evaporated to near dryness and re-dissolved in hexane. Polar components were removed by chromatographing on Bond-Elut silica columns (Analytichem International). The eluate was finally concentrated and analyzed for THC.

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

2.1.2. Determination of total hydrocarbon content (THC)

Total hydrocarbon levels were determined by gas chromatography (GC). Quantitation of THC was carried out by measuring the flame ionization detector response within the boiling range of n-C_{10} alkane to n-C_{22} alkane. The area was compared to the corresponding response of a known amount of the drilling mud base oil from BP (BP 83HF). Integrated areas were corrected for background levels from solvents (procedural blank).

The GC analyses were carried out under the following conditions:

Gas chromatograph : HP 5880 with HP auto sampler Mod 7671A
Column : 12.5 meter 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 : 290°
  Detector : 350°
  Carrier gas : Hydrogen
  Injection volume: 1.5 µl

Typical gas chromatograms are shown in Figures 3.1 to 3.4 along with the analytical results.

2.2. QUALITY ASSURANCE PROGRAMME FOR THE HYDROCARBON ANALYSIS

2.2.1. Preparations of samples and equipment

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

HPLC grade dichloromethane and hexane are used. Methanol is distilled over rectifying column (50 cm). Distilled solvent is kept in precleaned all glass container.

All equipment is rinsed with dichloromethane and heated at 600°C over night. Cleaned equipment is kept wrapped in aluminium foil.

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

2.2.2. Accuracy

The accuracy in the THC determination has been examined by comparing results obtained with the applied saponification method, and results obtained using ultrasonic extraction with CH_2Cl_2/MeOH, as well as 48 hours Soxhlet with CH_2Cl_2/MeOH. The three methods give comparable results when applied to sediments polluted by oily drill cuttings (R.G. Lichthenthaler, F. Oreld, S.P. Sporstøl, N.B. Vogt, "Evaluation of Chemical Methods for Monitoring of Hydrocarbon Discharges from offshore Installations", Proceedings of "Oil Based Drilling Fluids", SFT/Statfjord Unit Joint Research Project).

2.2.3. Reproducibility

The reproducibility of the analytical procedures was determined by analysis of sediment samples spiked with known amounts of oil.

From three replicate petroleum contaminated samples a relative standard deviation of 2.4 % was obtained for the individual THC results.

2.2.4. Detection and quantitation limits

According to the ACS Committee on Environmental Improvements ("Guidelines for Data Aquisition and Data Quality Evaluation in Environmental Chemistry", Anal.chem. 52(1980) p. 2242-2249) the minimum criterion for limit of detection (LOD) and limit of quantitation (LOQ) should be 3 s and 10 s above the measured average blank values, respectively..

Using these criteria the THC method has a LOD of 1.8 mg/kg and LOQ of 6.0 mg/kg.

3. MINERAL OIL MUD - RESULTS AND DISCUSSION

3.1. RESULTS

3.1.1. Total hydrocarbon content (THC) in sediments from the mineral oil mud (MOM) trays

The detailed results from the analysis of total hydrocarbon content in the sediment samples collected in the MOM trays are given in table 3.1.

At intervals (day 2, 9, 14, 21, 28, 49 and 88) three replicate samples have been taken for THC analyses. The samples were collected at random except for day 88. At day 88 two out of three samples were taken in the area with visible amount of cuttings. The third sample was taken in a "clean" area. This was the case for both the W 500 and W 5000 samples. At day 2 and day 88 the three samples were analysed separately. For the remaining samples the three replicates were pooled together before the THC analyses.

Typical gas chromatographic traces of sediment extracts from control tray, W 500 and W 5000 MOM trays are shown in Figures 3.1 to 3.3. Figure 3.1 contains the GC chromatogram of a sediment extract from the control tray, and Figure 3.2. a sediment extract from the W 500 tray. The gas chromatogram of the control does not show any typical oil profile and the inherent THC cause very little interference with the THC analysis of the MOM trays.

Figure 3.3. shows the gas chromatographic profile from the W 5000 tray. Figure 3.4. shows the gas chromatographic profile from the BP drilling mud base oil, BP83HF.

3.2. DISCUSSION

No significant change in total hydrocarbon content was observed.

In the W 500 sediments the concentration varies from 79 to 409 mg/kg dry sediment. This variation is not due to any degradation of the hydrocarbons, but simply reflects the unequal distribution of the cuttings in the tray. Lumps of cuttings were clearly visible, and at the end of the investigation, day 88, replicates from different areas both "contaminated" and "clean" were sampled.

The analytical results are in accordance with the observation, quite a lot of THC in the two "contaminated" samples and background level in the "clean" replicate. Similar results were obtained for the W 5000 sediments with a variation of the THC content from 897 to 6750 mg/kg dry sediment.

Based on the chemical analyses we may conclude that no degradation of hydrocarbons has occured in the present investigation.

Table 3.1.

TOTAL HYDROCARBON CONTENT (THC) IN SEDIMENTS FROM THE MOM TRAYS (mg/kg dry sediment)

Date	Days	W 500	W 5000	Control
21.6.90	2	103	1710	28
		156	3560	36
		79	6750	26
27.6.90	9	155	1940	
2.7.90	14	167	2740	
9.7.90	21	91	3270	
16.7.90	28	148	3450	
6.8.90	49	372	6320	
19.9.90	88	409	7260	28
		310	897	
		32	1320	

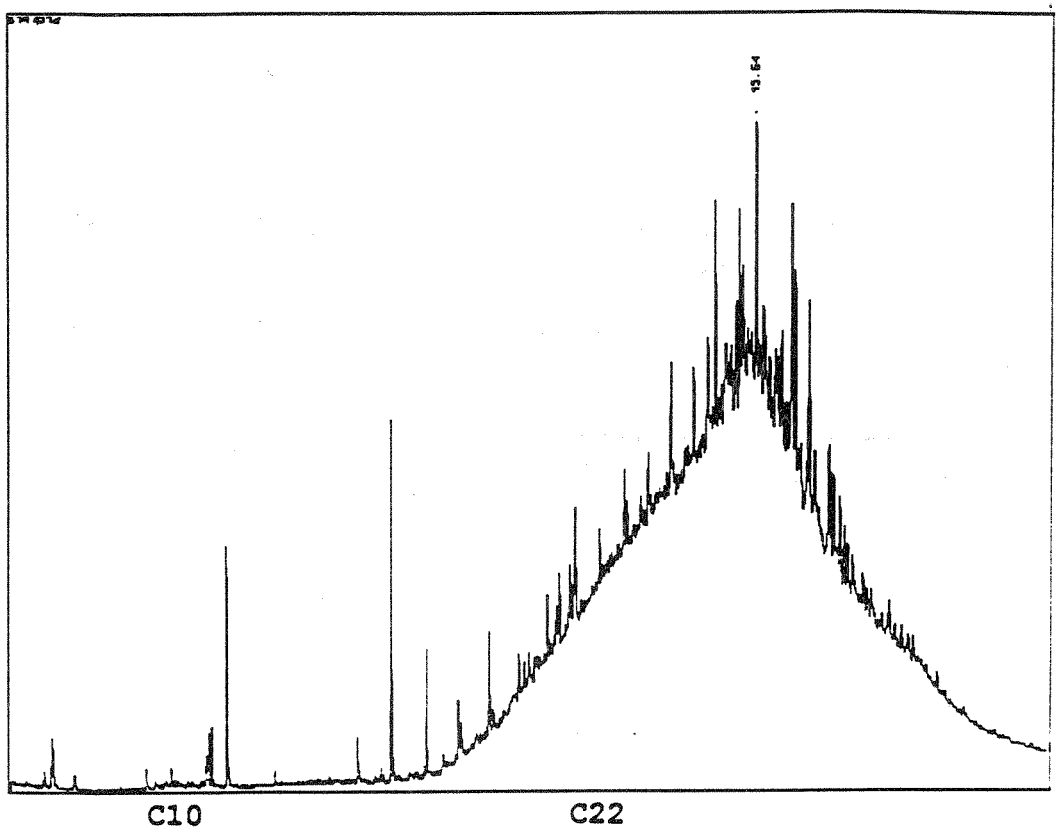

Figure 3.1.
GC chromatogram of the extract from the control tray

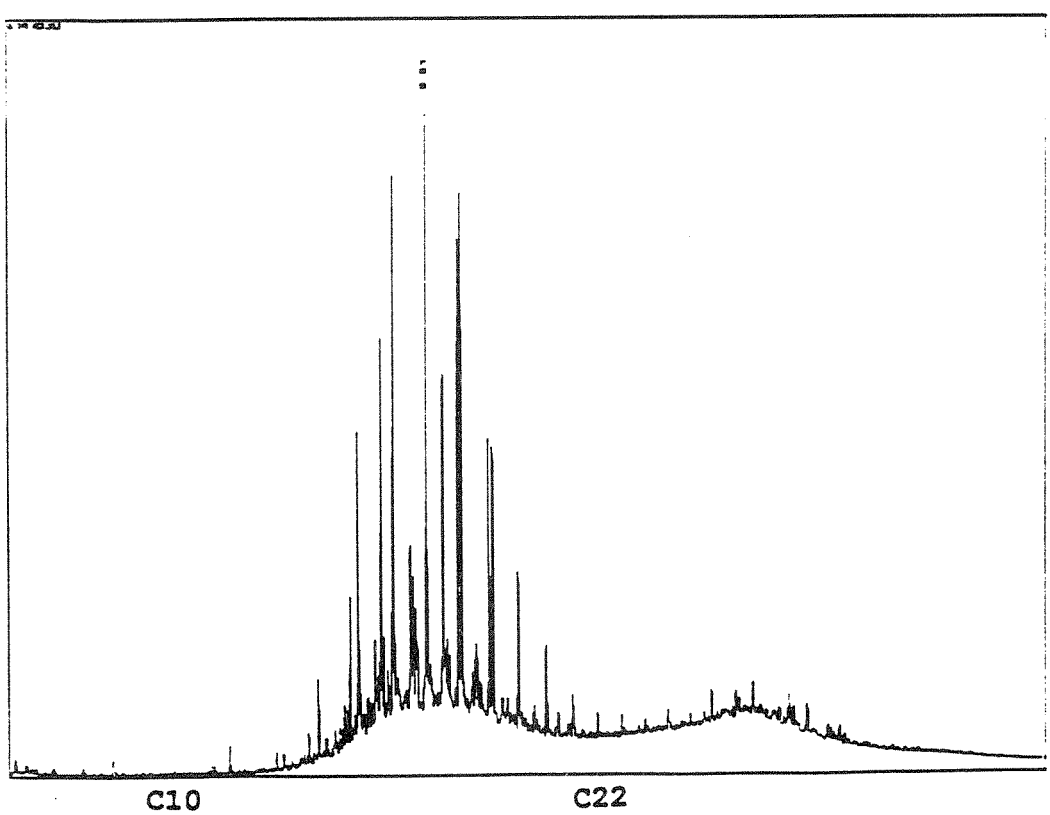

Figure 3.2.
GC chromatogram of the extract from the W 500 tray

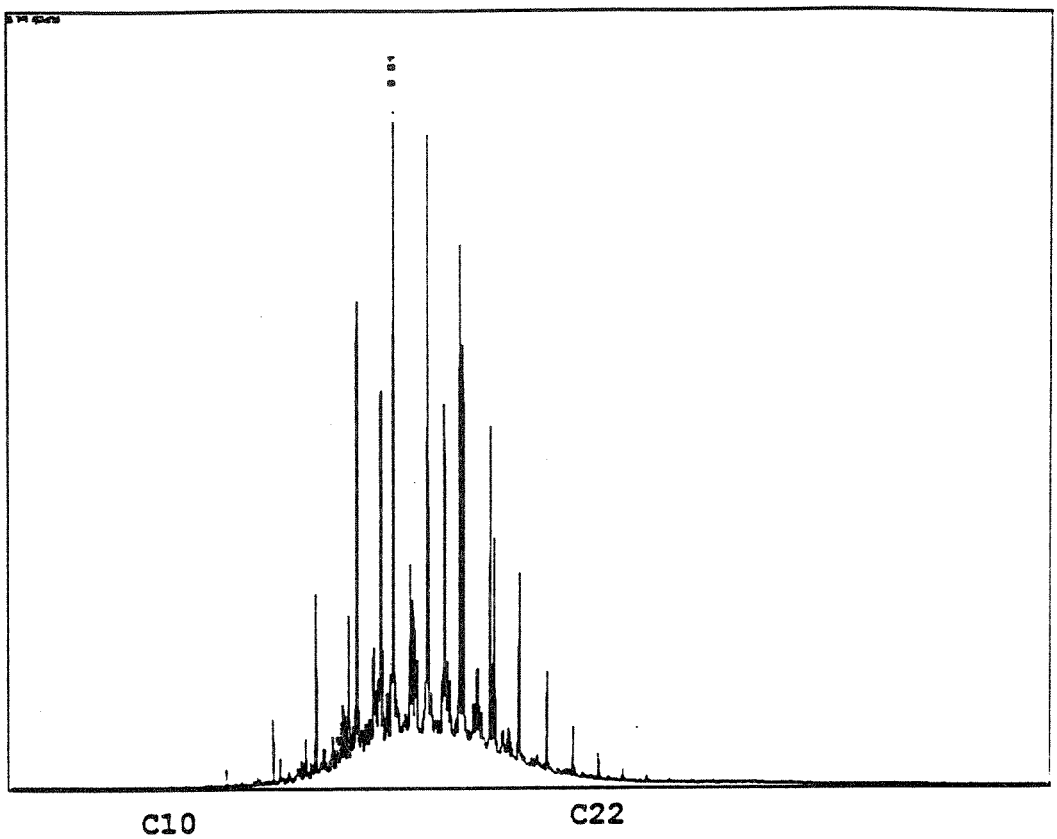

Figure 3.3.
GC chromatogram of the extract from the W 5000 tray

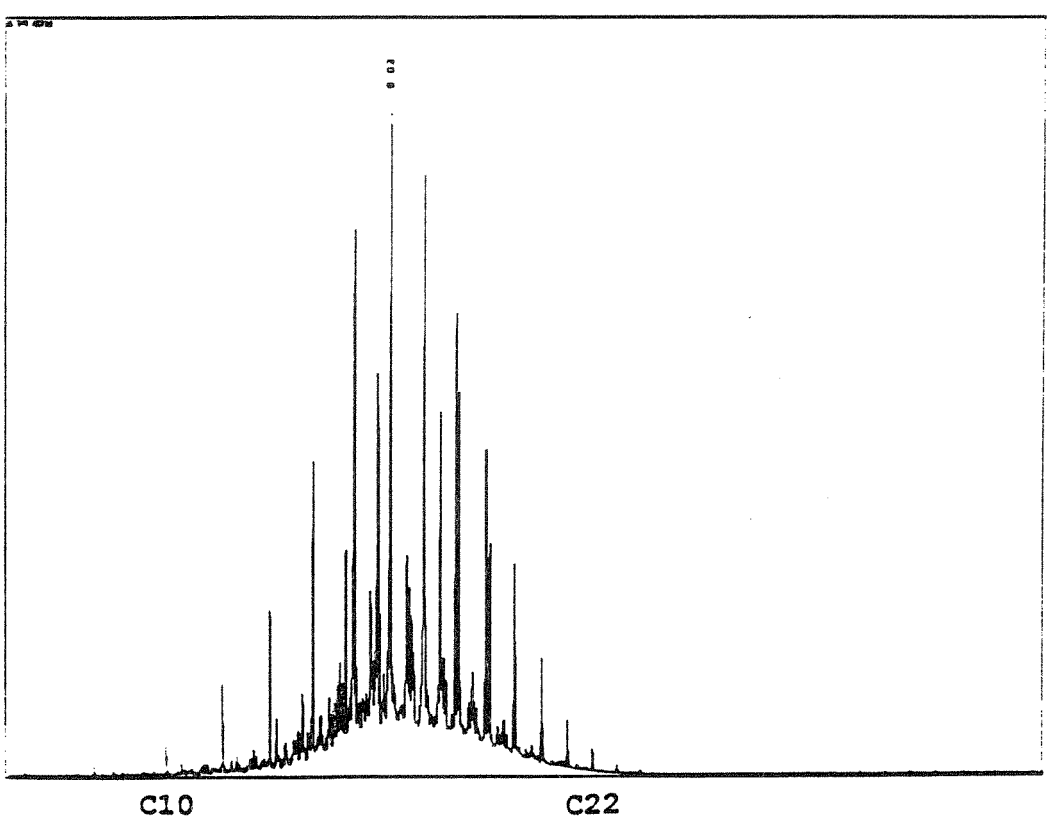

Figure 3.4.
GC cromatogram of the base oil, BP83HF

4. PETROFREE ESTER

DESCRIPTION OF THE ANALYTICAL PROCEDURE AND QUALITY ASSURANCE PROGRAMME FOR THE CHEMICAL ANALYSIS

4.1. ANALYTICAL PROCEDURE

4.1.1. Identity of Petrofree ester

A sample of the Petrofree ester was available from Baroid, and the chemical was analysed by computerized gas chromatography - mass spectrometry (GC/MS). This revealed a mixture of 5 homologous fatty acid esters. Their names and abbreviations are given below together with the internal standard used in the analyses.

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

4.1.2. Work-up procedure - Petrofree ester

The chemical analysis includes the determination of the Petrofree ester content. The Petrofree ester consists of five fatty acid esters. The two dominating compounds are 2-ethylhexyl dodecanoate and 2-ethylhexyl tetradecanoate. A detailed account of the quality assurance programme for the chemical analysis is given in section 4.2. below.

The sediment work-up procedure is based on a Soxhlet extraction method applied at the Herriot-Watt University in Scotland (Herriot-Watt, Statfjord Environmental Survey, June 1984, Report to Mobil Exploration Norway Inc.). Approximately 15-20 g of wet homogenized sediment was acidified with 0.1 M sulfuric acid and placed in a Soxhlet tube. Internal standard, ethyl stearate *), was added and the tube was refluxed with 300 ml methanol for 24 h. The methanol was then decanted and the sample was further extracted by refluxing with 300 ml dichloromethane. The methanol extract was diluted with 300 ml of water and extracted three times with dichloromethane (100+50+50 ml). The dichloromethane extracts were combined, washed with 2 x 100 ml of water and dried over Na_2SO_4. The sediment extracts were then evaporated to a suitable volume and analyzed for fatty acid ester.

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

*) 4 mg (P 500) and 40 mg (P 5000) were used for the samples from day 2 to day 28.
0.8 mg (P 500) and 20 mg (P 5000) were used for the samples from day 49 to 88.
0.08 mg (P500) and 2 mg (P5000) were used for the samples from day 178.

4.1.3. Determination of Petrofree ester

The content of Petrofree fatty acid esters in the sediment samples was determined by GC/MS analysis.

The mass spectra of the Petrofree compounds show several fragment ions with common masses available for quantitation. Among them m/z 112 was chosen for the quantitative determination of Petrofree. The mass spectrum of ethyl stearate (IS) shows a prominent fragment ion at m/z 88 which was chosen as the quantitation mass for this compound.

The quantitation was performed by using the Finnigan INCOS software which includes a user library option (LIBR) as well as a quantification program (QUAN). The following operations were performed:

The mass spectra of the 5 Petrofree compounds and the internal standard were obtained from a standard sample and included in a dedicated user library. Each of the 5 Petrofree entries were linked to the IS entry.

The amounts of each Petrofree compound in the standard sample was determined from the known total amount and the integrated areas of the reconstructed ion chromatogram (RIC), assuming equal response factors for the 5 compounds. The RIC is the sum of all m/z values in the MS scan range (m/z 35-400).

The amount information of Petrofree and IS was manually added to the user library by using the library editor (EDLB).

The retention time of the IS was obtained from the standard sample chromatogram and added to the user library.

A list of integrated areas (QUAN list) was constructed by integrating the m/z 88 (IS) and m/z 112 (Petrofree) ion chromatograms of the standard sample.

The relative retention time values as well as the response factors in the QUAN list from the standard sample was copied to the appropriate library entries.

An automatic data reduction procedure was set up which integrated m/z 88 and m/z 112 ion chromatogram time windows as specified by the library retention time information. The procedure also selected the largest peak in each window (X) which subsequently was quantified using the formula:

$$CONC_X = (AREA_{X,m/z\ 112} * CONC_{IS}) / (AREA_{IS,m/z\ 88} * RFACT._X)$$

The GC/MS analyses were carried out under the following conditions:

Gas chromatograph/mass spectrometer	: Finnigan 8200 dual magnetic electric sector instrument
Data system	: Incos 2300
Column	: 12.5 m x 0.2 mm i.d. fused silica. 0.32 µm methylsilicon (Ultra HP)
Temperatures:	
Column	: 50°C (2 min) - 10°C/min - 250°C (10 min)
Injector	: 250°C (split ratio 80 : 1)
Ion source	: 250°C
Linear gas velocity	: 44 cm/sec at 50°C (Helium)
Ionization	: Electron impact, 70 eV
Scan frequency	: 1 scan/0.6 sec
Scan range	: m/z 35-400
Ions for quantitation	: m/z 88 and 112

4.2. QUALITY ASSURANCE PROGRAMME FOR THE ANALYSIS OF FATTY ACID ESTERS (PETROFREE ESTER)

4.2.1. 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 hexane are used. Methanol is distilled over rectifying column (50 cm) and kept in precleaned all glass container.

The Soxhlet tubes were precleaned by cooking with both methanol and dichloromethane for 2 h.

All equipment is rinsed with dichloromethane and heated at 600°C over night. Cleaned equipment is kept wrapped in aluminium foil.

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

4.2.2. Recovery and accuracy

An internal standard was added to the sediment samples prior to the extraction procedure to compensate for losses during the sample preparation. To estimate the absolute recovery of the Petrofree compounds and the ethyl stearate (internal standard), an additional standard (d_{10}-pyrene) was added to selected samples after sample preparation but prior to GC/MS analysis. The absolute recovery of ethyl stearate (internal standard) was 79 $\pm$ 5.5 % for three replicate samples.

From three replicate "clean" sediments spiked with 50 mg (1200 ppm) of Petrofree ester an absolute recovery of 84 % was found. Due to the internal standard quantitation the accuracy of the method is improved, and a value of 105 % of the added amount was found for the three replicates.

4.2.3. Reproducibility

The reproducibility of the analytical procedures was determined by analysis of sediment samples spiked with known amounts of Petrofree ester. From three replicate Petrofree contaminated samples a relative standard deviation of 1.1 % was obtained for the individual Petrofree results.

4.2.4. Quantitation limit

In these experiments the quantitation limit was set to 5 mg/kg dry sediment. For future analyses of Petrofree ester it will be possible to improve the method and obtain a lower quantitation limit.

5. PETROFREE ESTER - RESULTS AND DISCUSSION

5.1. RESULTS

5.1.1. Content of fatty acid esters in sediments from the Petrofree trays

The detailed results from the analyses of the content of fatty acid esters in the sediment samples collected in the Petrofree trays are given in table 5.1.

At intervals (day 2, 9, 14, 21, 28, 49, 88 and 178) three replicate samples have been taken for Petrofree analyses. The samples were collected at random except for day 88 and day 178. At these two samplings two out of three samples were taken in the area with visible amount of cuttings. The third sample was taken in a "clean" area. This was the case for both P 500 and P 5000 samples. At day 2, day 88 and day 178 the three samples were analysed separately. For the remaining samples the three replicates were pooled together before the Petrofree analyses.

Figure 5.1. shows the GC/MS chromatogram of the Petrofree ester standard solution spiked with ethyl stearate (internal standard) and pyrene d_{10}. Figure 5.2. shows the GC/MS chromatogram of the same standard solution. In addition to sum of all ions scanned (RIC), ion chromatograms of Petrofree ester (m/z 112) and ethyl stearate (m/z 88) are also shown. Figures 5.3. to 5.7. show the mass spectra of the five fatty acid esters which represents the Petrofree ester. Figure 5.8. shows the mass spectrum of ethyl stearate (IS).

Typical GC/MS chromatograms of sediment extract with high Petrofree level (P 5000 day 88) and low Petrofree level (P 500 day 88) are shown in Figure 5.9. and 5.10. respectively.

5.2. DISCUSSION

Environmental surveys around the platforms in the North Sea has so far been limited to elements and hydrocarbons due to the use of oil based drilling mud. New types of drilling mud are now produced, and this will demand new analytical procedures dependent on the chemicals used.

In the present study the Petrofree mud consists of fatty acid esters. A suitable analytical programme was set out that would take care of the esters and their potential splitting to fatty acids and alcohol as well. The procedure includes continual extraction by both a polar and an unpolar solvent and instrumental analysis of the extract by GC/MS. Quantitation is performed by use of an internal standard added to the sediments prior to work up.

Notice that the analytical method for hydrocarbons includes saponification (breaking of the ester bond) and will thus be useless for the Petrofree ester.

The analytical procedure worked very well. For spiked samples at a concentration of 1200 ppm Petrofree ester, 105 % of the real value was found, and standard deviation of three replicates was 1.1 %. In addition GC/MS analysis gives a positive identification of the actual compounds.

The results from analysis of Petrofree ester listed in table 5.1. indicate that loss of fatty acid esters has taken place after 178 days of exposure.

In the P 500 sediments the concentration varies from < 5 to 2720 mg/kg dry sediment. This variation may not be due to any degradation of the fatty acid esters, but simply reflects the unequal distribution of the cuttings in the tray. This seems to be the situation up to day 28. (Unfortunately the P 500 sample from day 49 got lost during sample preparation).

After 88 days lumps of cuttings were still visible and replicates from both "contaminated" and "clean" areas were sampled. The analytical results are not quite in accordance with this observation as the first replicate from the P 500 tray was observed to be a "contaminated" sample and the analytical result was less than 5 ppm (background level). Also after 178 days lumps of cuttings were visible, and replicates from both "contaminated" and "clean" areas were again sampled. This time the analytical results were in accordance with the observation. The first sample was taken from a "clean" area and the analytical result was less than 5 ppm. In the two samples from the "contaminated" areas the content of petrofree ester was 63 and 45 ppm. Compared to day 2 one might draw the conclusion that some degradation has taken place.

In the P 5000 sediments the concentrations varies from 1530 to 11100 mg/kg dry sediment up to day 49.

After 88 days of exposure the two replicates from the observed "contaminated" areas contain less than 900 mg/kg dry sediment. The replicate from the "clean" area shows significantly low value. After 178 days of exposure the two replicates from the observed "contaminated" areas contain less than 100 mg/kg dry sediment. The analytical result from the "clean" sample was less than 5 ppm (background level).

The analyses and the observations from day 88 and day 178 indicate that some degradation of Petrofree ester has taken place.

No other compounds were detected that could originate from the esters.

Table 5.1.

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

Date	Days	P 500	P 5000	Control
21.6.90	2	58	9560	< 5
		15	5530	< 5
		2720	2340	< 5
27.6.90	9	13	10060	
2.7.90	14	< 5	3230	
9.7.90	21	< 5	1530	
16.7.90	28	616	11100	
6.8.90	49	*	2360	
19.9.90	88	< 5	587	< 5
		180	896	< 5
		< 5**	21**	
19.12.90	178	< 5**	< 5**	
		63	50	
		45	97	

* lost during sample preparation
** sample taken in a "clean" area

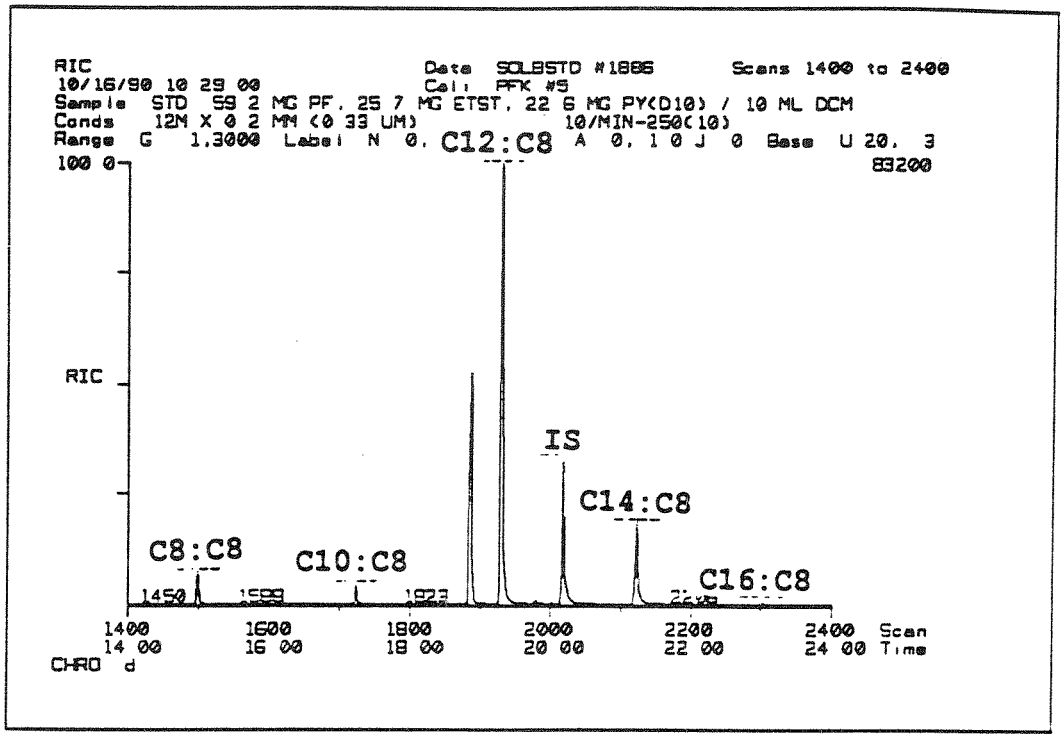

Figure 5.1.
GC/MS chromatogram of Petrofree standard solution

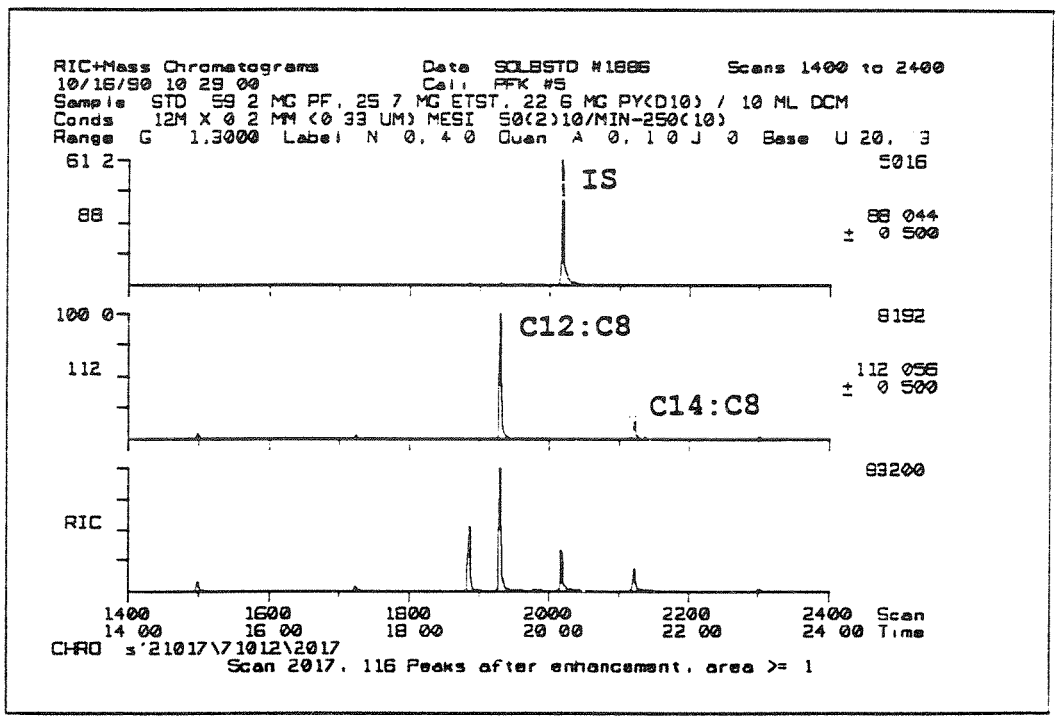

Figure 5.2.
GC/MS chromatogram of Petrofree standard solution. In addition to sum of all ions scanned (RIC), ion chromatograms of Petrofree esters (m/z 112) and ethyl stearate (internal standard, m/z 88) are also shown

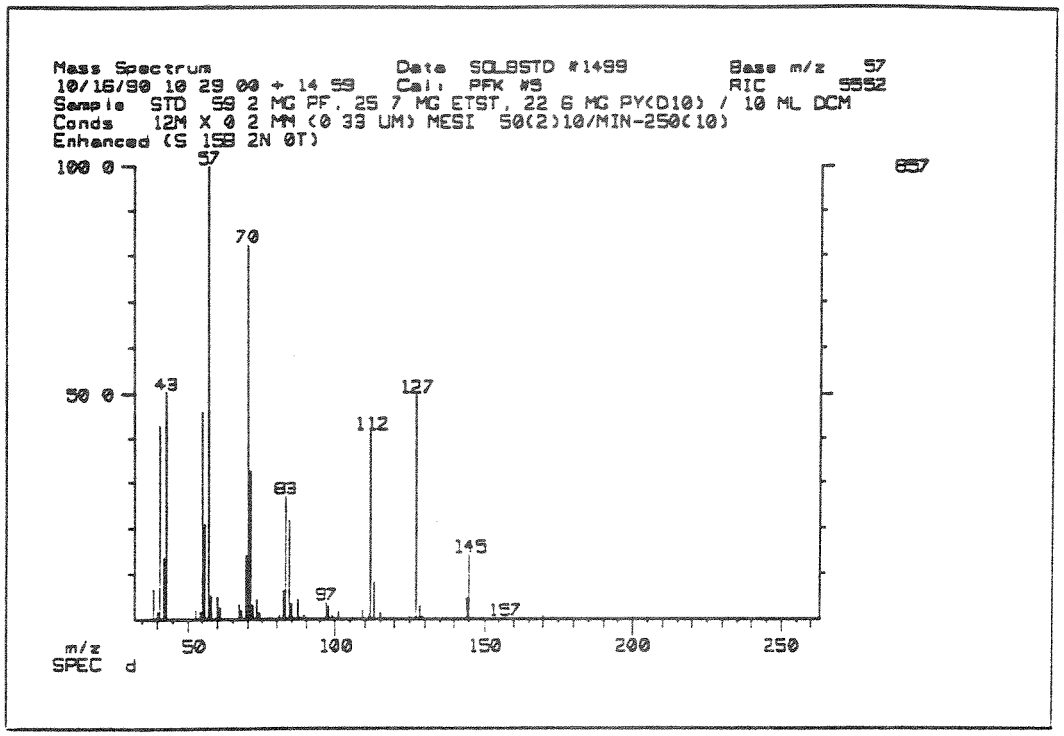

Figure 5.3.
MS spectrum of Petrofree ester 2-ethylhexyl octanoate (C8:C8)

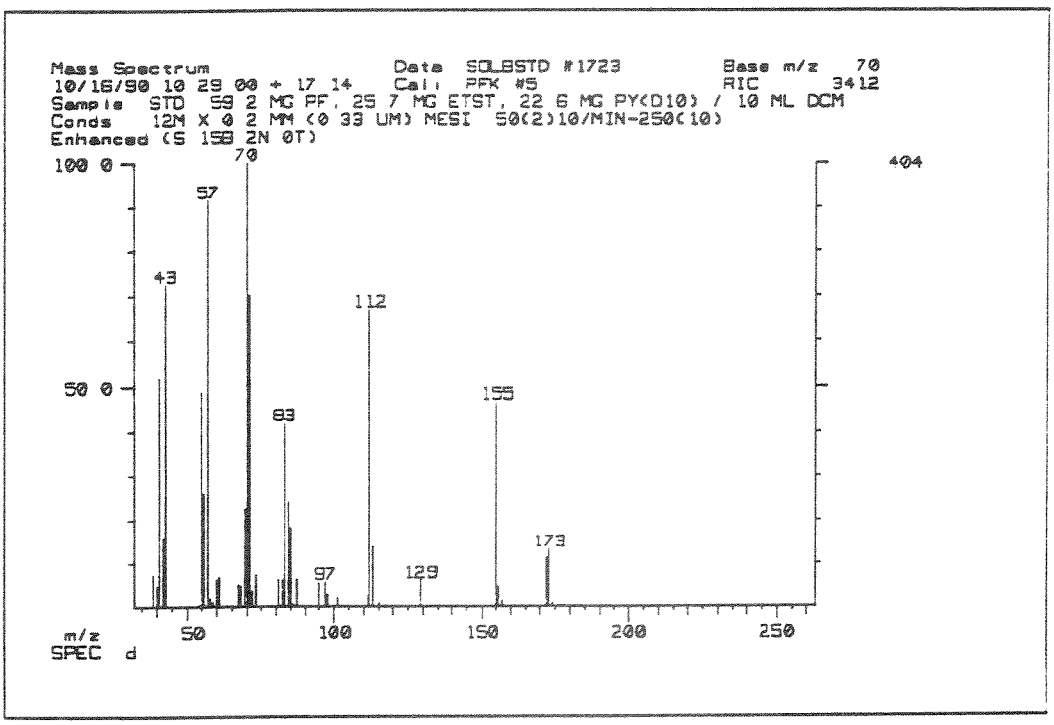

Figure 5.4.
MS spectrum of Petrofree ester 2-ethylhexyl decanoate (C10:C8)

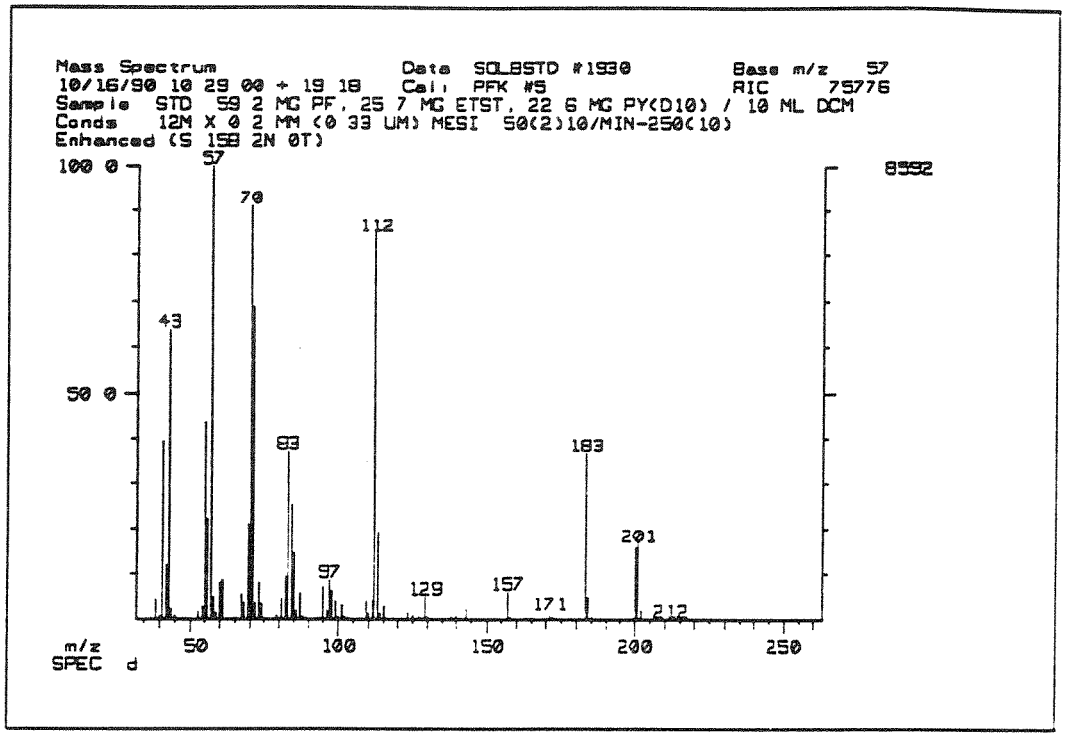

Figure 5.5.
MS spectrum of Petrofree ester 2-ethylhexyl dodecanoate (C12:C8)

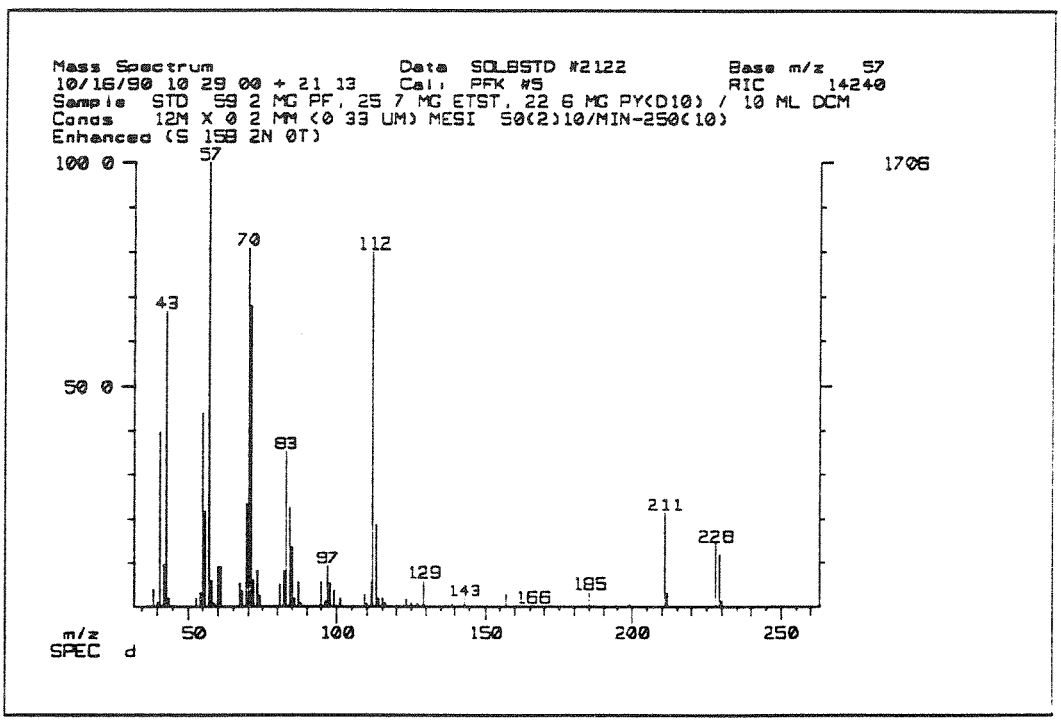

Figure 5.6.
MS spectrum of Petrofree ester 2-ethylhexyl tetradecanoate (C14:C8)

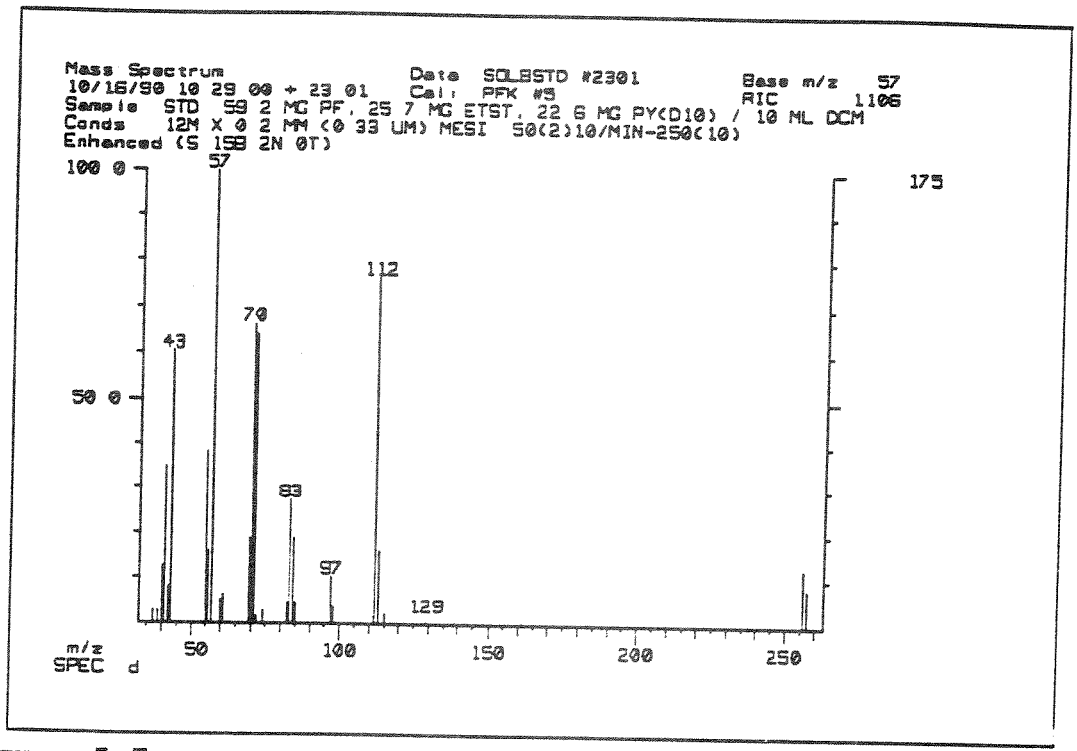

Figure 5.7.
MS spectrum of Petrofree ester 2-ethylhexyl hexadecanoate (C16:C8)

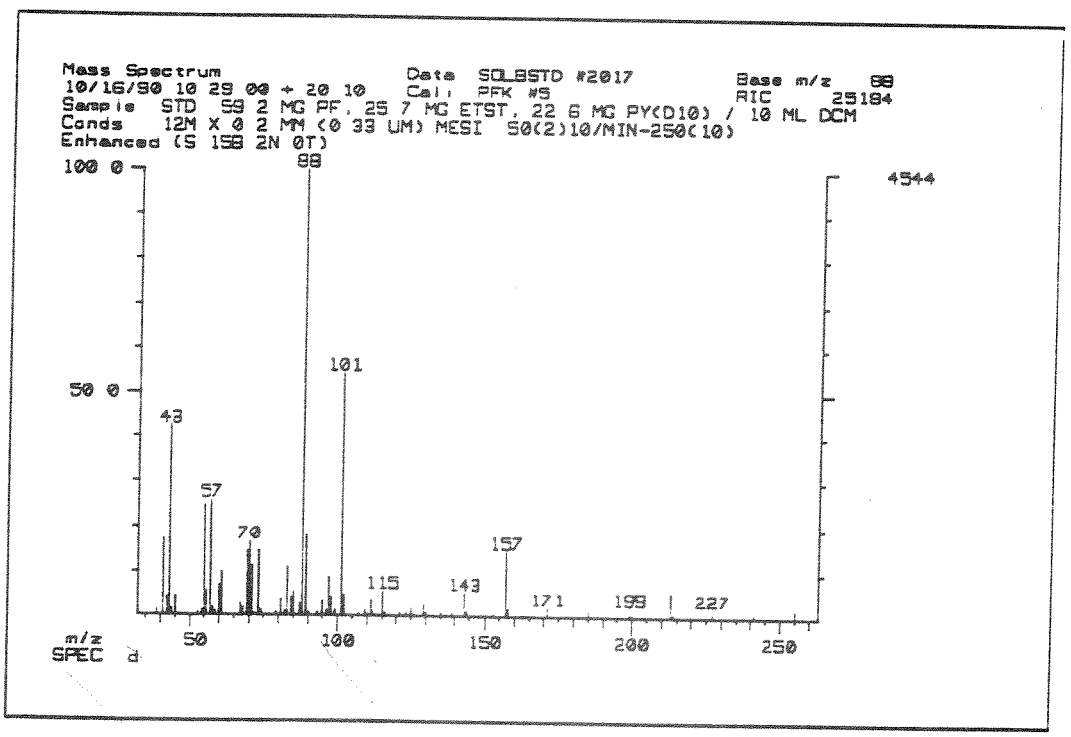

Figure 5.8.
MS spectrum of ethyl stearate (internal standard) (IS)

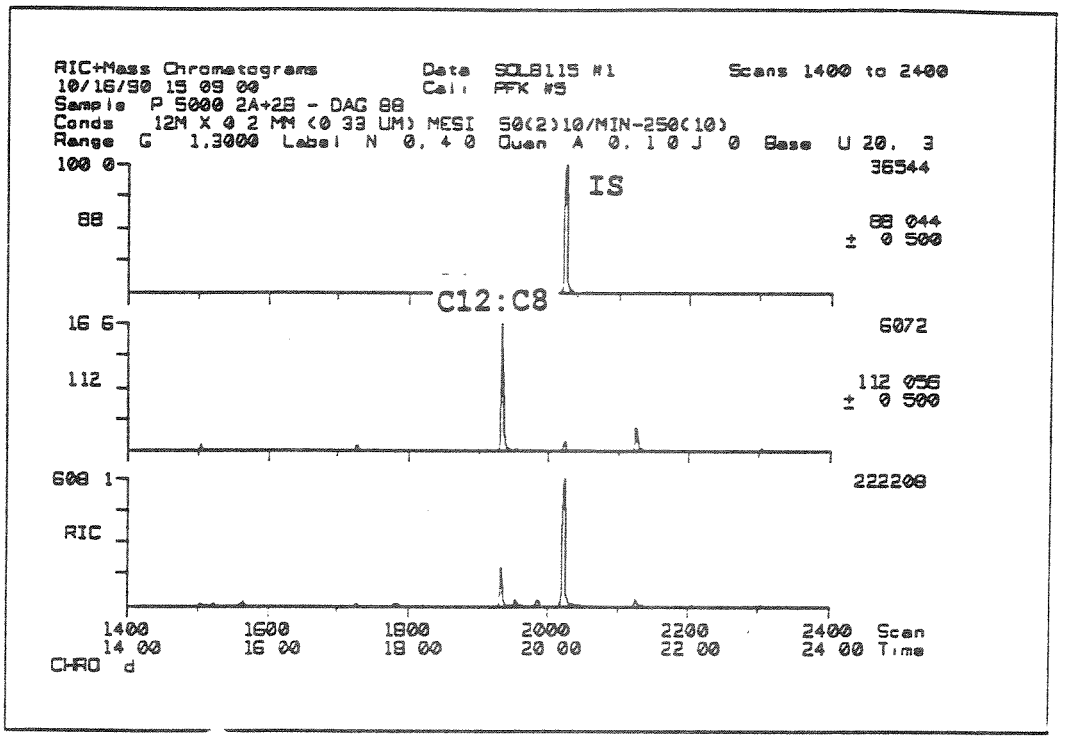

Figure 5.9.
Example of GC/MS chromatogram of sediment extract with high Petrofree level

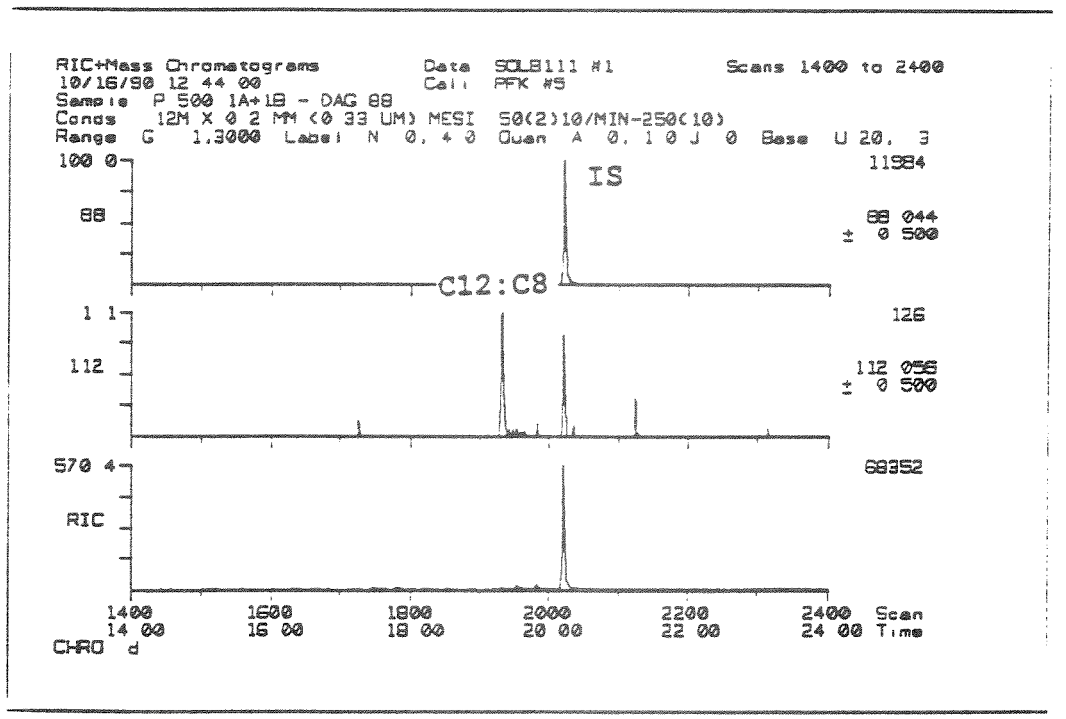

Figure 5.10.
Example of GC/MS chromatogram of sediment extract with low Petrofree level

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ISBN 82-577-1852-1