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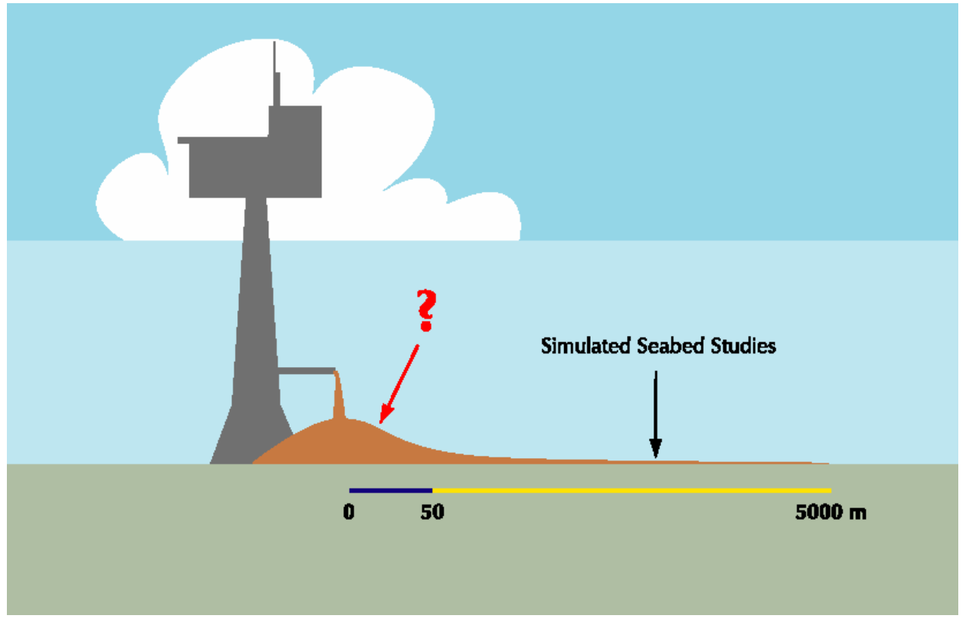
Remediation of sediments contaminated with drill cuttings

A review of field monitoring and experimental data for validation of the ERMS sediment module



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REPORT

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Abstract

During the period 1989-2004 biodegradation of the organic phase of drill cuttings have been investigated in the mesocosm laboratory at Marine Research Station at Solbergstrand. In this report, cross-test calculations of degradation rates for total hydrocarbons (THC) and poly-alpha-olefins (PAO) were compared with loss rates determined from off-shore monitoring data. Degradation rates for THC, PAO, more recently introduced olefins and esters were correlated with effects on biogeochemical and biological variables to provide a link with the sediment oxygen concentration modelled in ERMS.

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1. Borekaks	1. Drill cuttings
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ERMS - Enviromental Management Risk System

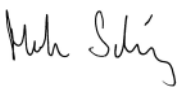
Remediation of sediments contaminated with drill cuttings

A review of field monitoring and experimental data for validation of the ERMS sediment module

Preface

This report is a contribution to the Enviromental Risk Management System (ERMS) activity "Validation of restitution calculations with ERMS sediment module". The report was prepared on request from Henrik Rye, SINTEF, in accordance with our proposal of 05.11.2004: "Factors affecting the restitution time for sediments contaminated by different types of drilling fluids (WBM, SBM, OBM) - Technical proposal for evaluation and systematic presentation of results from the Norwegian offshore monitoring and from experiments performed at the NIVA Marine Research Station Solbergstrand" and addendum described in our email of 14.03.05.

Oslo, 30.06.05



Morten Schaanning

Contents

Summary

The sediment module of the Environmental Management Risk System (ERMS) calculates effect thresholds and restitution times for off-shore sediments contaminated with drill cuttings. During the period 1989-2004 several mesocosm tests on the degradation and effects of organic based drill cuttings in bottom sediments has been performed at the Norwegian Institue for Water Research - NIVAs Marine Research Station at Solbergstrand. NIVA is also represented in a national expert group established by the Norwegian Pollution Control Authority (SFT) to evaluate the annual offshore environmental monitoring reports.

The present report provides a review of the mesocosm tests and new cross-test interpretations of degradation rates and effects on sediment oxygen consumption, redox potentials and diversity of macrobenthic communities. In addition, we have utilised historical monitoring data on total hydrocarbons (THC) and poly-alpha-olefins (PAO) from selected fields in the Norwegian sector of the North Sea to estimate in situ loss rates. Assuming first order decrease of sediment concentrations the monitoring data pooled for all selected fields gave half-lives of 0.8 years for THC and 1.4 years for PAO. This was fairly consistent with the cross-test analyses of the experimental data, which gave halflives of 0.5 years for THC and 0.8 years for PAO. Shorter half-lives of 0.03-0.19 years were found in mesocosm tests for the more recently introduced plant- or fish-oil esters and 14-16C olefins. The tests also showed that half-lives were slightly longer when determined in arctic communities at -1ºC than in Oslofjord communities at 8 ºC. A relatively strong increase of the degradation halflife was observed when the thickness of the cuttings layer was increased from about 1 mm to 8 mm.

The degradation rates determined for eight different organic phases could be correlated with the effects of the respective drill cuttings on sediment oxygen consumption, redox potentials and diversity of the macrobenthic communities. Thereby a link was established between the sediment oxygen concentrations modelled in ERMS and experimental data on effects on the macrobenthic community structure. The actual validation of the ERMS model will be performed by SINTEF.

The mesocosm experiments showed some recovery of biogeochemical variables within the six months experimental periods. Data on the recovery benthic macrofauna communities were only available from the field data which showed full diversity recovery within a period of 3 years after the discharge of THC contaminated cuttings had ceased.

1. Introduction

Discharge of solid waste (drill cuttings) from offshore drilling operations is often contaminated by an organic phase from the muds added to facilitate drilling. Most of the cuttings will sink to the bottom close to the drilling rig, where these deposits may remain for many years after drilling has been terminated. In old cuttings piles one may therefore still find remnants of oil based drilling muds (OBM) released prior to about 1992 when such discharges were prohibited on the Norwegian shelf. After that time, the discharges may be contaminated with other organic fluids such as ethers, esters and olefins developed to replace the mineral oil in OBM. Such discharges are often referred to as synthetic based muds (SBM). Water based drilling muds (WBM) are widely used, but do not contain such organic fluids. Recent experiments (Schaanning et al, 2005) have revealed a strong stimulation of seabed oxygen consumption after addition of WBM, probably due to the presence of minor amounts of a rapidly degrading organic phase.

The Norwegian Institute for Water Research (NIVA) has completed a large range of tests on the degradation of organic based drill cuttings in bottom sediments concurrent with studies on redox conditions and impact on bottom fauna. These experiments have been performed as “mesocosm” or “simulated seabed” studies at the Marine Research Station Solbergstrand. NIVA is also represented in a national expert group established by SFT to evaluate the annual offshore environmental monitoring reports, and advice SFT in establishment of guidelines for such monitoring at the Norwegian shelf. Controlled experiments with replication and comparison to reference conditions give high reproducibility and fairly precise comparison between the various drilling fluids.

Experimental conditions will, however, deviate from the natural shelf seabed. In particular the thickness of the layers of added cuttings was small and the duration of the experiments were short compared to the time series obtained from field monitoring. Furthermore, the seabed environment in many offshore field locations is more dynamic with periods of strong bottom currents which are difficult to simulate in experimental work. Therefore, seabed remediation by resuspension and horizontal sediment transport may be more important in the field than in mesocosm simulations. The test results should therefore be evaluated against relevant results from the offshore monitoring, to achieve data as realistic as possible for use in modelling.

2. Material and methods (mesocosm experiments)

2.1 Outline of test set-ups and environmental conditions

The overall degradation rates of organic drilling fluids on cuttings have been experimentally determined in "simulated seabed" studies performed at NIVAs Marine Research Station Solbergstrand located by the Oslofjord, SE Norway, outside the sill at Drøbak. The various tests are outlined in **Table 1**. Tests 1-4 were performed on mixed sediments from the Oslofjord. Tests 4-10 were performed on undisturbed sediments transferred from 110-120 m depth in the outer Oslofjord using 50 x 50 cm or 32 x 34 cm box core liners. Test 11 was performed in 10 cm (ID) sediment cores.

The tests were run in well oxygenated water continously supplied from the water inlet at 60 m depth in the fjord nearby. The salinity and temperature of this water rarely vary beyond 33-35 and 6-9°C. In test 9 additional box core samples were transferred from 120 m depth in Roddenesjøen (Raaddenjargsjøen). The temperatures in this semienclosed basin near the head of the Porsangen fjord, N.Norway, is <0ºC during most of the year. During sample collection in March 1997, the salinity and temperature of the bottom water was 34.0 and -1.15°C. In the mesocosm, these samples were maintained in Oslofjord water from 60 m depth cooled to -0.5°C.

After 1-3 weeks of equilibration in the mesocosm, the organic phase from various drilling muds were added by mixing laboratory made cuttings (mud or organic phase soaked onto dried marine clay sediments) or cuttings sampled from offshore drilling operations with sea water. The slurries were then mixed into the overlying water in each box and allowed to settle in thin layers on top of the sediments. Normal layer thickness was 1-2 mm, normal dose was 3-4 mg cm^{-2} of the organic phase, or about 5000 ppm averaged over the 0-1 cm layer. In test 10 the chemicals were added in 8.0 mm frozen sheets of cuttings diluted in marine clay sediments. Test periods varied 25-273 days, but were mostly about six months. Throughout the test period, the overlying water was continuously exchanged with fjord water. O_2 concentration was regularly measured and never allowed to decrease below 50% saturation.

Sediment samples for chemical analyses were collected from the experimental boxes in small cores (ID 1.5-4 cm) to include the sediment down to at least 3 cm depth. Downwards mixing of the organic phase by the organisms present in the experiments never provided significant amounts of organic phase below this depth (disregarding the thick layers in test 11). In tests 5-10, samples were collected taking 1.5 cm (ID) syringe core samples from 3-5 random locations within the box area. The cores were sectioned at 3 cm depth and pooled into a preweighed 50 ml glass jar. Total wet weight of the samples were determined during sampling. In the laboratory, the organic phase was extracted from a sub-sample of the wet sediment. The concentration of the organic phase was calculated from:

Equation 1: $$\mathbf{C_a = I_{GC} \cdot M_s / M_{GC} \cdot n \cdot A_{core}}$$

in which:

- C_a = concentration of organic phase ($mgOP \cdot cm^{-2}$)
- I_{GC} = integrated GC peak area, corrected for reagent blank (mgOP in extract)
- M_{GC} = mass of sub-sample for extraction (g wet sediment)
- M_s = total mass of sediment sample (g wet sediment)
- n = number of cores
- A_{core} = area of each core sample

In tests 1-4 the sediment was sampled using a slightly different procedure and the results from some of these tests has been recalculated from mg kg^{-1} dry sed. to mg cm^{-2} using more or less accurate assumptions on water content and sediment density.

Table 1. Experiments performed on biodegradation of the organic phase of various drilling muds on cuttings at the Marine Research Station at Solbergstrand.

Test no.	Organic phase	Nos. and size of exp. units	Initial conc. mg OP·cm^{-2}	Layer mm	Dur-ation days	Reference
1	Mineral oil	5 x 0.5 m^2	0-50	0.05-2	175	Bakke et al, 1989
2*	Plant oil ester	3 x 0.5 m^2	3.5	1	227	Bakke og
	Mineral oil	3 x 0.5 m^2	2	2		Laake, 1991
3*	Ether	1 x 0.5 m^2	2	2	273	Laake et al ,1992
	Mineral oil	1 x 0.5 m^2	10	2		
4	Olefin C16-C32	2 x 0.5 m^2	2.2-11.5	0.2-1.5	212	Schaanning og
	Mineral oil	1 x 0.5 m^2	5.3	1.4		Laake, 1993
	Plant oil ester	1 x 0.5 m^2	3.5	1.2		
5	Ether	2 x 0.25 m^2	12.6-13.3	2.8	150	Schaanning, 1994
	Mineral oil	2 x 0.25 m^2	2.5-2.7	1.1		
	Plant oil ester	2 x 0.25 m^2	4.1-4.2	1.2		
6	Olefin C20	2 x 0.25 m^2	6.5-10.5	1	161	Schaanning, 1996
	Ether	2 x 0.25 m^2	12.2-17.6	1		
	Plant oil ester	2 x 0.25 m^2	13.1-18.5	1		
7	Olefin C14-C16	4 x 0.25 m^2	2.5-3.4	1	176	Schaanning, 1995
	Olefin C20	1 x 0.25 m^2	1.7	1		
	Plant oil ester	1 x 0.25 m^2	2.4	1		
8	Fish oil ester	2 x 0.25 m^2	5.7-6.6	1.4-1.7	187	Schaanning
	Olefin C16-C18	2 x 0.25 m^2	3.6-4.5	3.6-4.5		*et al.*, 1996
	Olefin C14-C16	2 x 0.25 m^2	3.8-4.0	1.4-1.7		
	Plant oil ester	2 x 0.25 m^2	4.2-4.3	1.7-1.9		
	Mineral oil	2 x 0.25 m^2	1.9-2.2	1.7-1.9		
9	Fish oil ester	6 x 0.25 m^2	0.5-20	0.1-4.0	89	Schaanning
	Olefin C14-C16	6 x 0.25 m^2	0.5-20	0.1-4.0		*et al.*, 1997
10	Fish oil ester	6 x 0.1 m^2	4.5-5.7	8.0	214	Schaanning
	Olefin C14-C16	3 x 0.1 m^2	4.5	8.0		and Rygg, 2003
	Mineral oil	3 x 0.1 m^2	7.7	8.0		
11	Waterbased	12 x 78 cm^2	unknown	0.4-45	25	Schaanning *et al.*, 2005

*Additional low dose treatments not cited in this work.

2.2 Chemical analyses

2.2.1 Organic phase

All chemical analyses of organic phase has been performed and partly developed at the SINTEF (c.f. Oreld and Gjøs, 1995) or NIVA laboratory in Oslo. Exact procedures may have varied between laboratories and tests and details may have deviated from the general description below.

Mineral oil was extracted by saponification in 0.5 M methanolic KOH under reflux for 2 hours, filtered and washed with 50 ml methanol and extracted twice with dichloromethane. The dichloromethane extracts were washed with water and dried over sodium sulfide (Na_2SO_4), evaporated and re-dissolved in hexane. Polar components were removed by chromatographing on Bond-Elut silica columns and the eluate was concentrated and analysed for total hydrocarbons (THC) by gas chromatography (GC). Samples for analyses of ethers, esters and olefins were extracted with methanol in Soxhlete tubes for 2.5 hours and further with dichloromethane for 17 hours. In tests 6-10 the Soxhlete extractions were replaced with extraction in ultrasonic bath. The dichloromethane extracts were washed with 2x50 ml of water and dried over Na_2SO_4 before evaporation to a suitable volume (5-25 ml) and analyses by GC.

Background levels were controlled by analyses of procedural blanks and minimised using carefully rinsed equipment and analytical grade chemicals. Quantitation of the components was carried out by measuring the flame ionisation detector (FID) response of the area of the components of interest. For all components, an appropriate internal standard was added to the sediment samples prior to the extraction. The recovery of the internal standard was normally > 95%. The reproducibility (relative standard deviation of repeated analyses) of the analytical procedures was normally within ±2%.

2.2.2 Barium

Barium was analysed with x-ray in subsamples dried for 48 hours at 105ºC. Barium was analysed in all samples from tests 6-9.

2.3 Degradation model

First order kinetics have been found most appropriate for the description of the loss of drilling fluids with time and have also been found applicable to field sites in the North Sea (Daan et al, 1995). The general form of the model is:

Equation 2 $$\mathbf{C = C_0 \cdot e^{-kt}}$$

in which:

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

From the equation above, it can be shown that if the half-life, τ, is the time at which $C = C_0/2$, then $\tau = \ln 2/k$. Regression analyses on ln transformed loss data were performed in JMP™ statistical analyses software, which yield best fit estimates and standard errors on the intercept (C_0) and slope (k). For the cross-test comparisons performed in this work, C was replaced with concentrations normalised against

initial concentration. For tests 6-9, C was replaced with the organic phase (OP) to barium (Ba) ratio and normalised against the initial ratio: (OP:Ba):(OP_0:Ba_0). Barium normalisation will reduce the scatter due to patchy distribution of cuttings and has not been found to have any systematic impact on half-life estimates.

2.4 Organic phase characterisation

The organic phase was characterised by GC/MS analyses performed at the SINTEF and NIVA laboratories during first time tests on the respective mud product.

The plant oil ester was found to be a mixture of five homologous isopropyl esters, made up from saturated C8-C16 fatty acids (Oreld *et al*., 1991). The main component was 2-ethylhexyl dodekanoate.

The fish oil ester was a mixture of isopropyl esters of saturated and unsaturated C14-C22 fatty acids (Schaanning *et al*., 1996).

The ether was an alkyl ether with the stoichiometric formula $C_{20}H_{42}O_2$ (Gjøs et al., 1992, Oreld and Gjøs, 1994).

The first olefin product (Olefin C16-C32) tested in 1992, was a mixture of branched C16, C24 and C32 polyalphaolefins of which C24 was the predominant component and C32 the second most abundant (Oreld and Gjøs, 1993).

A later product (Olefin C20) was found to be a saturated hydrocarbon with the chemical formula $C_{20}H_{42}$ (Oreld and Gjøs, 1995). The chromatograms indicated a highly branched structure.

Frequent branching was also found in the Olefin C16-C20. The composition was confirmed by GC/MS to be unsaturated hydrocarbons (olefins, mostly with one double bond) with varying number of carbon atoms and fractions decreasing C16>C18>C20 (Schaanning *et al*., 1996).

The most frequently tested Olefin C14-C16 was a mixture of C14 and C16 olefins with C14 slightly more abundant in early samples changing towards C16 dominance in samples collected towards the end of the sampling periods (Oreld and Gjøs, 1995).

3. Degradation of organic phases

3.1 Mesocosm experiments

3.1.1 Loss mechanisms

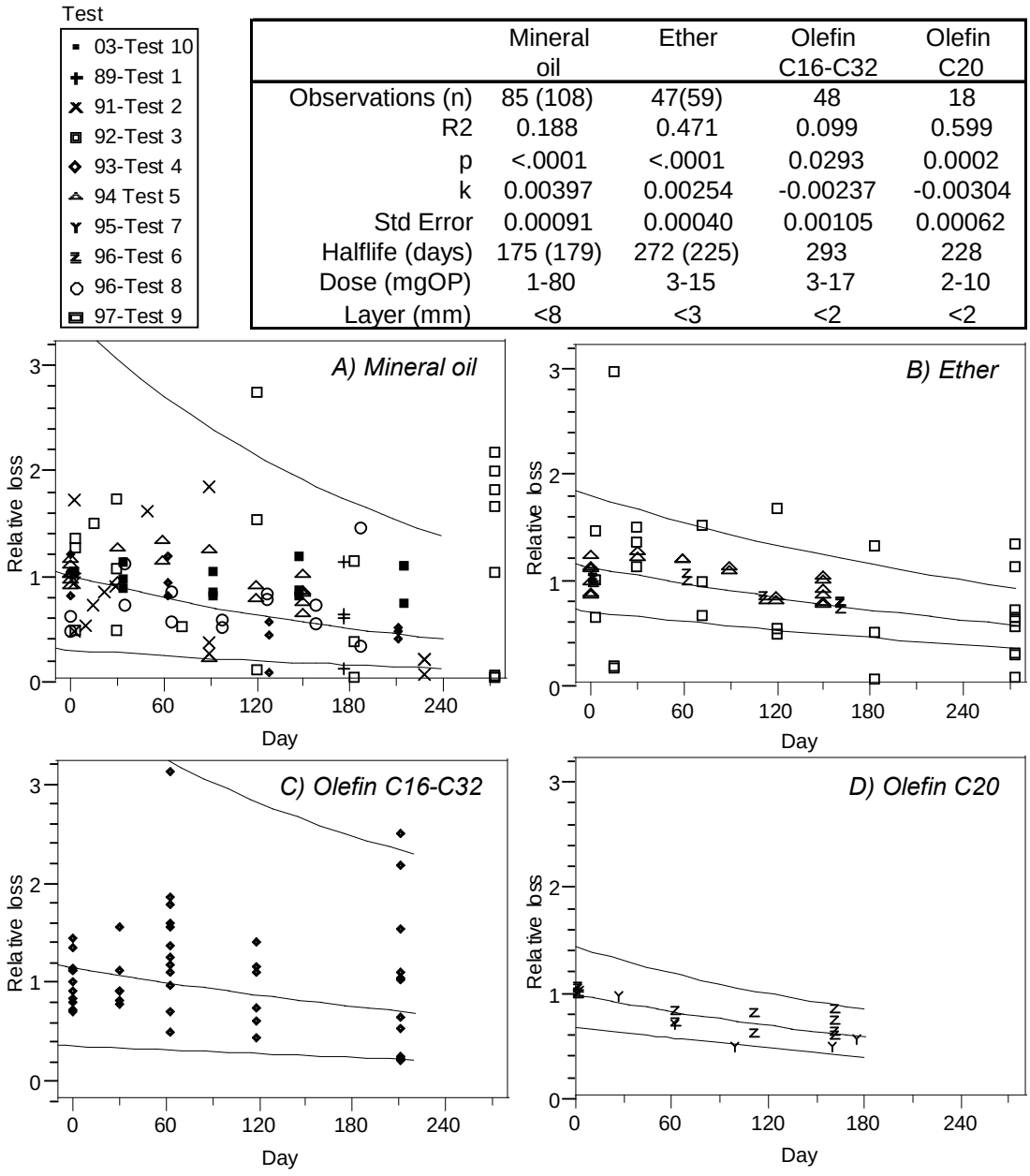
The organic phase may be lost from the test sediments by dissolution or resuspension into the water flowing through the boxes as well as via biodegradation. Generally low loss of barium showed that resuspension and burial beyond sampling depth contributed little to the observed decrease of organic phase concentration. The organic phase is closely associated with the mineral fraction of drill cuttings. The amount of organic phase recovered from the sediment surface 1-2 days after addition was generally consistent with the amounts added and no evidence was ever found that the organic phase was lost by dissolution during test set-ups. Sediment oxygen consumption was always low shortly after addition, but generally increased during the first 1-2 weeks of the experiment, presumably due to a growing community of bacteria associated with organic phase degradation. Also, significant loss of organic phase from the sediments was always associated with a preceding period of elevated rates of O_2 uptake from the water. Thus, it can be concluded that biodegradation was the predominant mechanism accounting for the observed decrease of concentration of organic phase in all tests performed. However, mass balance calculations have shown that the amount of oxygen consumed could only account for 20-80% conversion of the organic phase carbon to CO_2. The discrepancy may be accounted for by sulphate reduction and incomplete reoxidation of the H_2S produced and /or formation of metabolites not detectable by the GC analyses performed. Alternatively the metabolites might be more soluble and disappear by dissolution into the overlying water.

3.1.2 Loss rates

Results of the cross-test regression analyses on all data grouped by organic phase are shown in **Figure 1** and **Figure 2**. Poor model fits ($R^2 \leq 0.1339$) were obtained for mineral oil, ethers and C16-C32 olefins. However, as shown in **Figure 1** A and B, the scatter was particularly large in test 3 due to extremely patchy distribution of cuttings on the experimental surface with concentrations ranging 0.05 - 4 times initial concentrations after 280 days. Both disposal and sampling techniques were improved to reduce scatter in subsequent tests. Disregarding all test 3 data on mineral oil (n=23) p was reduced from 0.0004 to <.0001, the standard error decreased from 0.00106 to 0.00091 and the halflife changed by 4 days. For ether, test 3 data were disregarded by omitting six pairs of maximum and minimum concentrations on day 15, 29, 120, 180 and 273 (2 pairs) in the regression analyses. This reduced p from 0.0044 to <.0001, reduced the standarrd error from 0.00104 to 0.00040 and increased the half-life from 225 to 272 days.

The decrease with time was always significant ($p<0.05$) confirming that all organic phases tested are to some extent degradable. However, with regard to the four organic phases shown in **Figure 1**, the upper confidence limit curves showed that we cannot predict at the 95% significance level that a sample collected within the time span of the experiments performed will contain less than initial concentration.

The data for the more degradable olefins and esters are shown in **Figure 2**. Olefin half-lives decreased with decreasing carbon chain length from 293 days for C16-32 to 75 days for the C14-C16 olefins. The most rapid degradation rates were found for the esters with half-lifes of 25 days for the plant oil esters and 34 days for the fish oil ester. Considering the high number of samples and relatively broad range of experimental conditions, the curve fits were quite good with correlation coefficients (R^2) of 0.476-0.720 and $p<0.0001$. By the end of the experimental periods, the upper confidence limits was



	Mineral oil	Ether	Olefin C16-C32	Olefin C20
Observations (n)	85 (108)	47(59)	48	18
R2	0.188	0.471	0.099	0.599
p	<.0001	<.0001	0.0293	0.0002
k	0.00397	0.00254	-0.00237	-0.00304
Std Error	0.00091	0.00040	0.00105	0.00062
Halflife (days)	175 (179)	272 (225)	293	228
Dose (mgOP)	1-80	3-15	3-17	2-10
Layer (mm)	<8	<3	<2	<2

Figure 1. Relative loss of A) mineral oil, B) ether, C) Olefin C16-C32 and D) Olefin C20 in sediment samples collected 0-230 days after deposition of cuttings in mesocosm experiments. Lines display best fit curves for exponential degradation ($C = C_0\ e^{-kt}$) and 95 % confidence limts for an individual predicted value. The analyses were performed on concentrations normalised to initial concentration ($OP:OP_0$) or OP:Ba concentration ratio ($(OP:Ba):(OP_0:Ba_0)$). Range of initial concentration (mgOP cm^{-2}) and layer thickness is inserted together with results of the regression analyses. Due to scatter in test 3 all data on mineral oil and 6 concurrent pairs of highest and lowest concentrations of ethers were omitted. Total number of analyses and half-lives obtained from the full data set are shown in brackets in the table.

	Olefin C16-C20	Olefin C14-C16	Plant oil ester	Fish oil ester
Observations (n)	16	64	80	56
R2	0.707	0.476	0.720	0.599
p	<.0001	<.0001	<.0001	<.0001
k	-0.00749	-0.00928	-0.02721	-0.02053
Std Error	0.00129	0.00124	0.00192	0.00228
Halflife (days)	93	75	25	34
Dose (mgOP)	3-5	1-17	4-17	1-17
Layer (mm)	<2	<8	<2	<8

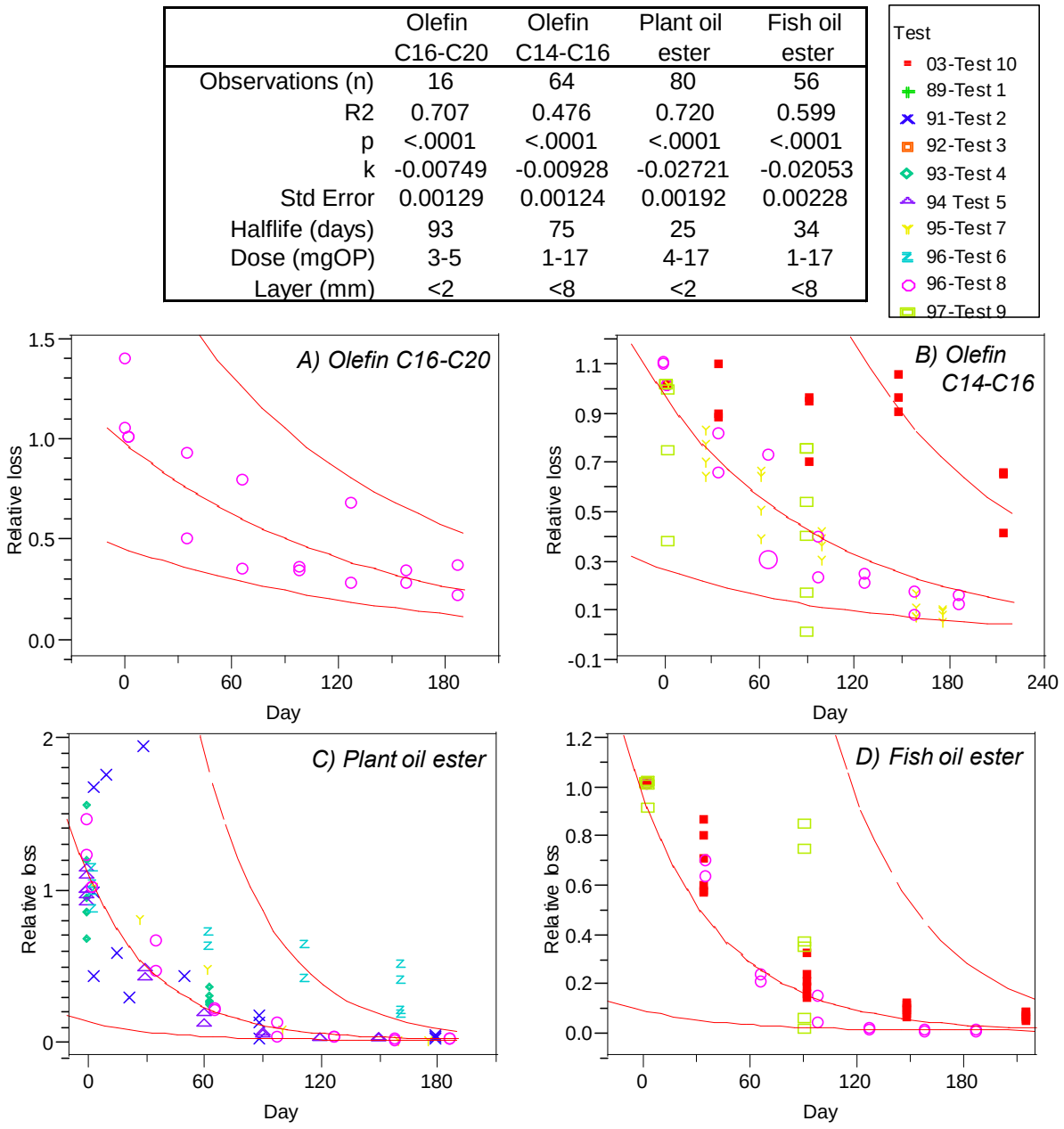


Figure 2. Relative loss of A) Olefin C16-C20, B) Olefin C14-C16, C) Plant oil ester and D) Fish oil ester in sediment samples collected 0-230 days after deposition of cuttings in mesocosm experiments. Lines display best fit curves for exponential degradation ($C = C_0\ e^{-kt}$) and 95 % confidence limts for an individual predicted value. The analyses were performed on concentrations normalised to initial concentration ($OP:OP_0$) or OP:Ba concentration ratio ($(OP:Ba):(OP_0:Ba_0)$). Range of initial concentration (mgOP cm^{-2}) and layer thickness is inserted together with results of the regression analyses.

50-60% of initial concentration for the two olefins and 10-15% for the esters. Thus, different from mineral oil, ethers and long-chain olefins, degradation of the four organic phases shown in **Figure 2** was unquestionable within the time span of our experiments.

3.1.3 Water based mud

In test 11, cuttings with water based mud was added in various layer thickness to sediment cores (ID=10cm). Neither benthic community nor chemical analyses were undertaken in this experiment. Thus neither harmfull effects nor the identity or amount of organic phases present in these cuttings have been documented. However, sediment oxygen consumption was measured twice a week for 25 days after addition (**Figure 3**) and oxygen profiles in the sediment were determined 20 days after addtion of the cuttings (**Figure 4**). The latter gave no evidence for the presence of hydrogen sulphide in the sediments, but oxygen penetration had been reduced from a maximum depth of 5 mm in the control core to 1 mm in the core treated with cuttings.

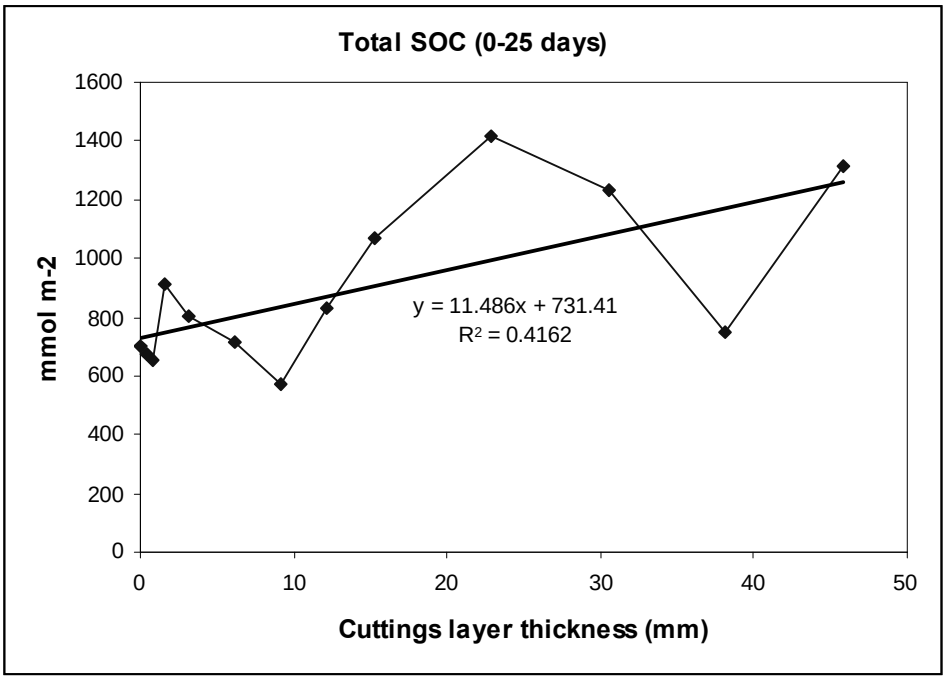


Figure 3. Cumulative sediment O_2 consumption in cores with increasing layer thickness of cuttings sampled from a drilling operation with water based mud. O_2 consumption peaked 2-15 days after addition of the cuttings, indicating rapid degradation of a small amount of an organic phase. Data from test 11.

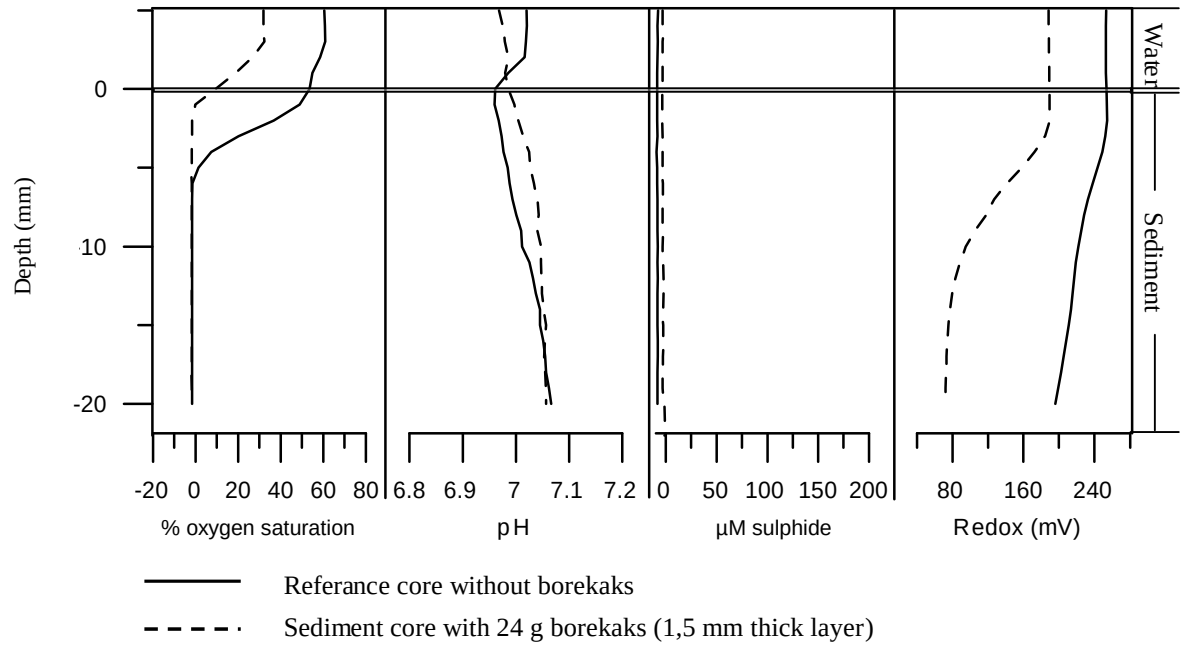


Figure 4. Micro-electrode profiles across the sediment-water interface in control core with no cuttings added and in a core treated with 1.5mm layer of water based cuttings. The profiles were measured 20 days after addition of cuttings. Data from test 11.

A short peak of O_2 consumption occurred 2-15 days after addition, with maximum consumption rates up to 3.2 mol O_2 m^{-2} h^{-1} or about 10x higher than control cores with no cuttings added. During final sampling on day 25, elevated consumption rates were only observed in the high dose cores with 31 and 46 mm thick layers of cuttings. This indicated the presence in the water based cuttings of a rapidly degrading organic phase. Simultaneous proliferation of black spots in the sediments below the cuttings layer indicated that the organic phase was available for degradation by sulphate reducing bacteria. Due to sulphide toxicity, negative impacts on sediment-dwelling animals are likely to occurr during deposition of such cuttings, but oxidation and/or precipitation of the H_2S produced during degradation will most likely detoxify the sediments within a relatively short period of time after the operation is finished.

3.1.4 Effects of dose and layer thickness

The relationship between dose and effects on degradation rates have not been systematically approached in the present experiments. In tests 1, 3, 4, 5 and 6, the dose added exceeded 8 mg OP cm^{-2} in several treatments with layer thickness <4 mm. In test 10 the cuttings were diluted with sediments in 8 mm thick layers with dose <9 mg OP cm^{-2}. Thus groups of data with normal ranges of both dose and layer could be compared with groups of high dose and/or groups with thick layers (**Table 2** and **Table 3**). The latter table shows that the degradation constant decreased with both

Table 2. Regression analyses on data grouped according to dose and layer thickness.

	Dose	Layer	Halflife		Regeression analyses ($C=C_0e^{-kt}$)				Data
	mg cm^{-2}	mm	days	n	R^2	p	k*1000	std error *1000	Test no.
Mineral oil	3.7	1.5	130	66	0.269	<.0001	5.32	2.10	1,2,4,5,8
Mineral oil	16.7	2.4	190	46	0.076	0.0638	3.64	1.91	1,3,4
Mineral oil	7.7	8.0	2636	15	0.023	0.5916	0.26	0.48	10
Ether	2.9	2.0	245	27	0.082	0.1475	2.83	1.89	3
Ether	12.4	2.1	422	32	0.407	<.0001	1.64	0.36	5,6
Olefin 16-32	3.4	0.2	127	24	0.383	0.0013	5.48	1.48	4
Olefin 16-32	17.4	1.5	(-942)	24	0.027	0.4427	-0.74	0.94	4
Olefin 20	1.7	1.0	164	6	0.762	0.0233	4.22	1.18	7
Olefin 20	8.2	1.0	286	12	0.647	0.0016	2.43	0.57	6
Olefin 14-16	3.3	1.2	48	40	0.899	<.0001	14.36	0.78	7,8
Olefin 14-16	4.5	8.0	300	15	0.475	0.0045	2.31	0.67	10
Fish ester	6.6	1.6	20	26	0.780	<.0001	35.29	3.82	8,9
Fish ester	5.1	8.0	47	30	0.925	<.0001	14.86	0.80	10
Plant ester	4.5	1.3	22	68	0.901	<.0001	32.11	1.31	2,4,5,7,8
Plant ester	16.5	1.0	90	12	0.760	0.0002	7.68	1.37	6

Table 3. Effects of dose and layer thickness on the rate consant (k*1000) ± 1 std. error. Data from Table 2.
N = normal range of dose and layer.
D = high dose, normal layer.
L = normal dose, thick layer.

	N	D	L
Mineral oil	5.3±2.1	3.6±1.9	0.3±0.5
Ether	2.8±1.9	1.6±0.4	-
Olefin 16-32	5.5±1.5	-0.7±0.9	-
Olefin 20	4.2±1.2	2.4±0.6	-
Olefin 14-16	14.4±0.8	-	2.3±0.7
Plant ester	32.1±1.3	7.7±1.4	-
Fish ester	35.3±3.8	-	14.9±0.8

dose and layer thickness. 3-5 times increase of mean dose gave a corresponding decrease of plant oil ester k from 32.1±1.3 to 7.68±1.4 (k*1000). The relative decrease was less for mineral oil (5.3±2.1 to 3.6±1.9), ether (2.8±1.9 to 1.6±0.4) and olefin C20 (4.2±1.2 to 2.4±0.6). Increased layer thickness had a strong impact and resulted in no significant degradation of mineral oil (k*1000=0.3±0.5) and slow degradation of olefin C14-C16 (14.4±0.8 to 2.3±0.7). The impact of layer thickness on the fish oil ester appeared less strong, but a clear reduction was observed from 35.3±3.8 to 14.9±0.8.

Oxygen penetration in sediments are restricted to a few mm below the sediment water interface (Revsbech et al, 1980, DiToro, 2001 and **Figure 4**) and depend on the consumption rate within the surface layer. Therefore organic phases and degradation bacteria present in layers of about 2 mm or less are likely to have much better access to O_2 supplied from the seawater than organic phases present in the lower part of an 8 mm thick layer. This also means that organic phases available to anoxic degradation, i.e. primarily sulphate reduction, will be less hampered by thick layer deposits than organic phases which are less available to such processes. Esters degrade by hydrolytic cleavage of the ester bond to produce alcohols and fatty acids. The fatty acids are easily available for uptake in living cells and will undergo rapid β-oxidation in cell mitochondria. Sediments treated with ester-based cuttings generally stimulated sulphate reduction more strongly than the olefins. If olefins are less available than esters for anaerobic degradation (Eriksen *et al.*, 2002), layer thickness should slow down degradation of olefins more strongly than esters, as observed (**Table 3**).

Another possible factor contributing to increased halflives in test 10 (8 mm layer), may have been the frozen sheet technique used in this setup only. Freezing might slow down the development of microbial communities capable of degrading the respective organic phases. The olefins are presumably more xenobiotic than the fatty acid esters and mineral oil hydrocarbons, and may consequently be more sensitive to initial disturbance of the microbial communities. On the other hand, growth rates for bacterial communities are frequently on the orders of hours-days and the degradation rate was measured regularly over an experimental period of seven months. Therefore, freezing to -20°C may inhibit initial degradation rates, but is not likely to be responsible for the large slow-down of degradation rates integrated for the seven months experimental period.

Reduced availability of oxygen may result either from thicker cuttings layer (slower diffusive transport) or higher concentration of chemical (more rapid O_2 consumption). Therefore, increasing the dose without increasing the layer thickness will also reduce oxygen availability and degradation rate. In addition, allthough no clear evidence has been found, it may be speculated that toxicity might contribute to a slower degradation in layers with high concentration of organic phase. Both olefins and esters are low-toxic substances, but questions have been raised about the toxicity of the alcohol produced by ester hydrolysis. Thus, it is possible that ester or alcohol toxicity contributed to the strong dose impact on the degradation constant of the plant oil ester. Wether this would be similar for the fish oil ester which is naturally more abundant in the seabed environment than the plant oil ester is neither confirmed nor rejected by the available data.

3.1.5 Effects of low temperature

In test 9, biodegradation of the 14C-16C olefin and the fish oil ester was compared by additon to sediment communities from the Oslofjord location as well as from an arctic basin. The Oslofjord communities were maintained in the mesocosm at 6-9ºC and the arctic communities were maintained at -1 ºC. It is important to recognize that other factors than temperature may have contributed to differences between the two test sediments. The communities from the different locations differed with regard to macrobenthic community. In particular, the presence of a large (3-4 cm) sea urchin bioturbator (*Ctenodiscus crispatus*) may have affected degradation by its shuffling activity providing frequent redistribution of the cuttings and increasing oxygen availability from the overlying water. This specie was present in the arctic sediments only and no species in the Oslofjord sediment had a similar activity pattern. Also, the arctic location was a pristine location less influenced by anthropogenic activity and presumably less adapted to hydrocarbon and other contamination than the Oslofjord sediments.

Cuttings were distributed to the sediments in three doses, 0,5, 5 and 15 mgOP cm^{-2} and with different layer thickness 0.1, 1 and 4 mm, respectively. As shown in **Figure 5**, the degradation constant tended to decrease with decreasing temperatures (i.e. slower degradation), but to various extents. In the low dose treatments the data from the Oslofjord were uncertain due to not detectable amounts remaining in the sediment at the final sampling. In the high dose treatments, little degradation was observed in either treament. The results for low and medium dose of olefins and high dose of ester was not widely different from a doubling of the k-value for the 9 ºC difference in temperature. A doubling of rates for each 10 ºC increase of temperature is a frequently used thumb-nail rule for metabolic rates, and the present experiment gave no reason to reject the validity of this relationship for the two drilling mud phases tested at the low end of the range of sea water temperatures. Thus, degradation rates of the organic phases were more strongly affected by molecular structure, concentration and layer thickness, than differences in temperature and benthic community structure of the seabed environment.

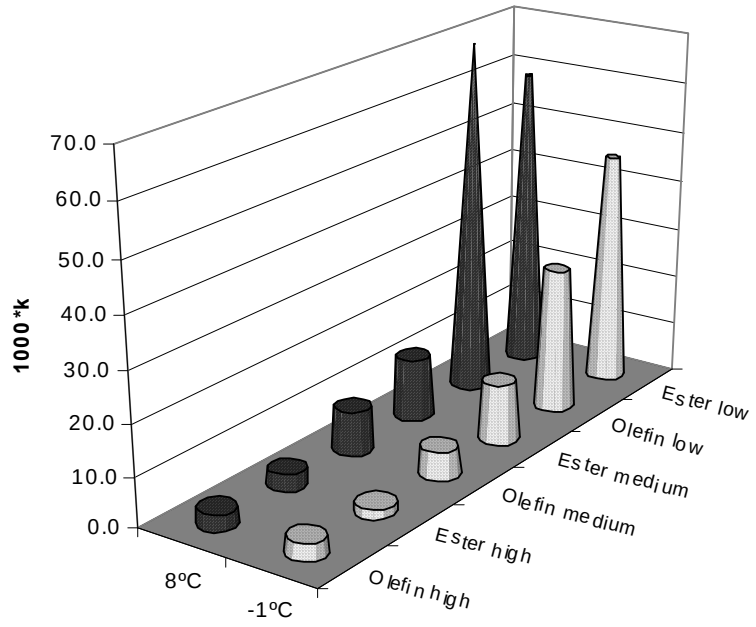


Figure 5. Effects of temperature on degradation rate for olefin 14C-16C and fish oil ester at three different dose levels.

3.2 Half life estimates from field monitoring data

We have utilised historical monitoring data on total hydrocarbons for selected fields in an attempt to estimate *in situ* degradation rates. The basis for selection of fields, time periods and stations was the following:

- Data should be available for at least two years, preferably a longer time series
- Available information on cuttings discharge history should suggest that no new discharges of oil or synthetic based cuttings had occurred during the time span selected.
- The stations should show a significant THC contamination in year zero. Normally this limited the station selection to those at 1000 m or closer to the field centre.
- The stations should not show an increase in THC level over time (indicative of new input of THC).

Under these criteria we selected the fields listed in **Table 4** as basis for the degradation estimates of THC and PAO. These were the only base fluids parameters for which field data existed which were considered reasonably unconfounded by other discharges. The data used were extracted directly from the monitoring reports and put into EXCEL worksheets. For the THC concentrations we subtracted an assumed common background value of 10 mg/kg to obtain net concentrations of cuttings related THC.

Table 4. Offshore fields, time periods, number of stations and distance range used for the base fluid degradation rate calculations.

Field	Time span	Number of surveys	Number of stations	Distance range (m)	Parameter used
Valhall	1996-2002	3	2	1000	THC
Varg	2000 - 2003	2	2	250 - 500	THC
Statfjord A	1988 – 2002	10	8	250 – 1000	THC
Statfjord B	1996 - 2002	3	7	250 - 1000	THC
Statfjord C	1996 - 2002	3	7	250 - 1000	THC
Gullfaks C	1991 - 1996	5	3	250 - 1000	THC
Gullfaks C	1996 - 2002	3	3	250 - 1000	THC
Gyda	1988 - 2002	6	7	250 - 1000	THC
Tordis	1996 - 2002	3	5	250 - 1000	PAO
Frøy	1997 - 2003	3	9	250 - 1000	PAO

For each station at each field the THC concentrations were normalised against year zero (expressed as %THC of the year 0 concentration). An example of the change in THC over time is given for the Gyda field in **Figure 6**. The figure shows no systematic relationship between initial concentrations and rate of loss in relative THC over time.

Then a simple regression analysis between year and %THC across all stations and surveys for each field were constructed (**Figure 7**). From the fitting of an exponential relation to this regression (assuming the same exponential loss from degradation as for the experimental data) the half lives of the base fluid were estimated. The same was done for the PAO-contaminated fields (**Figure 8**). Global regression analyses on THC and PAO, pooling all data from the individual fields treated was also made (**Figure 9**).

In addition to the exponential model used, we also calculated the half lives from the models that showed the best fit to the individual regression patterns.

Normalisation of THC against barium, as has been done in the experimental work, was not attempted since the discharges of THC (or PAO) and barium have no consistent connection in the field. Barium may be discharged from other sources, e.g. water based muds applied in the same area.

The results of the regression analyses and half life estimates are shown in **Table 5**. The exponential half-lives for THC ranged from 0,4 to 3,2 years for individual fields. Pooling all THC data into one regression analysis gave an exponential half life of 0,8 years with a 95 % confidence interval for new observations of 0 – 5,2 years.

The two estimates on PAO degradation rates gave exponential half lives in the range 0,8 – 1,7 years. Pooling the data gave an exponential half life of 1,4 years. The best fit model gave slightly higher half life estimate of 1,8 years (95% confidence limits for new observations: 0 – 6,5 years).

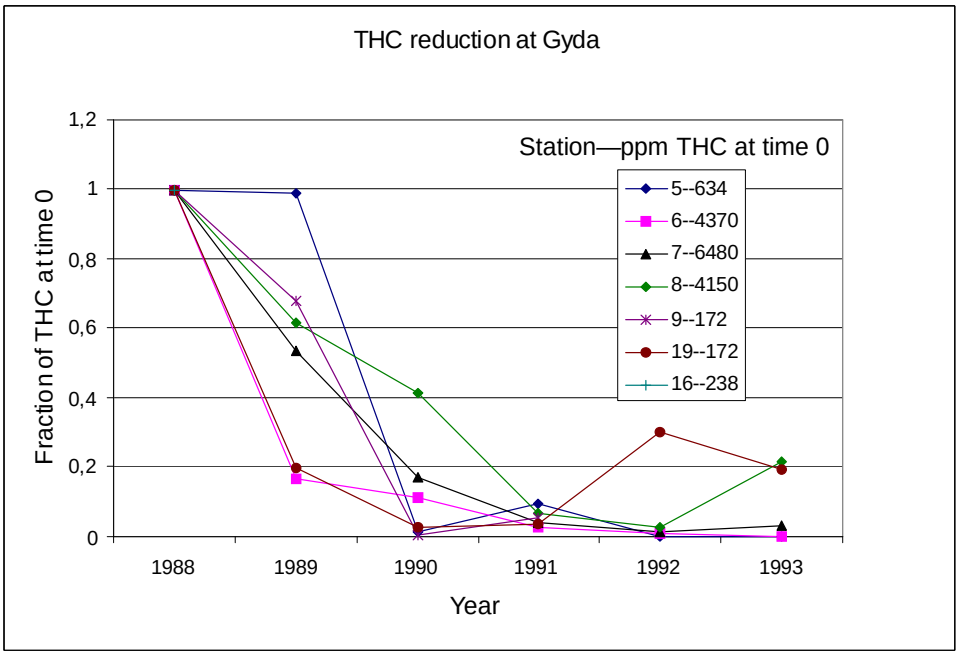


Figure 6. Change in relative concentration of THC in the upper 1 cm at 7 monitoring stations around Gyda from 1988 to 1993. The absolute concentrations in 1988 (year 0) are indicated in the legend.

Table 5. Results of regression analyses and half life estimated for THC and PAO at the fields selected.

Field	**R^2 for the exponential model (%)**	**Half life (year)**	**Best fit model**	**R^2 for the the best fit model**	**Half life from best fit model (CI for individual samples)**
Valhall	84,9	1,7	Sqrt(year)	96,1	1,7 (1,1 – 2,3)
Varg	89,4	0,8	Exponential	89,4	0,8 (0 – 3)
Statfjord A	47,8	1,4	Sqrt(year)	52,1	2,6 (0,1 – 5,3)
Statfjord B	12,2	3,2	Sqrt(%THC)	26,5	3,9
Statfjord C	51,9	2,7	Sqrt(year)	71,2	2,5 (0,1 – 5,4)
Gullfaks C 91-96	47,9	0,4	Sqrt(year)	74,4	1,1 (0 – 2,8)
Gullfaks C 96-02	80,7	2,1	Exponential	80,7	2,1 (0 – 5,1)
Gyda	42,9	0,3	Sqrt(year)	77,3	1,0 (0 – 3,1)
All with THC	**26,5**	**0,8**	**Exponential**	**26,5**	**0,8 (0 – 5,2)**
Tordis (PAO)	48,4	0,8	Sqrt(year)	81,7	1,6 (0 – 5,4)
Frøy (PAO)	65,1	1,7	Sqrt(%THC)	68,6	2,5 (0 – 5,4)
All with PAO	**54,6**	**1,4**	**Sqrt(year)**	**76,4**	**1,8 (0 – 6,5)**

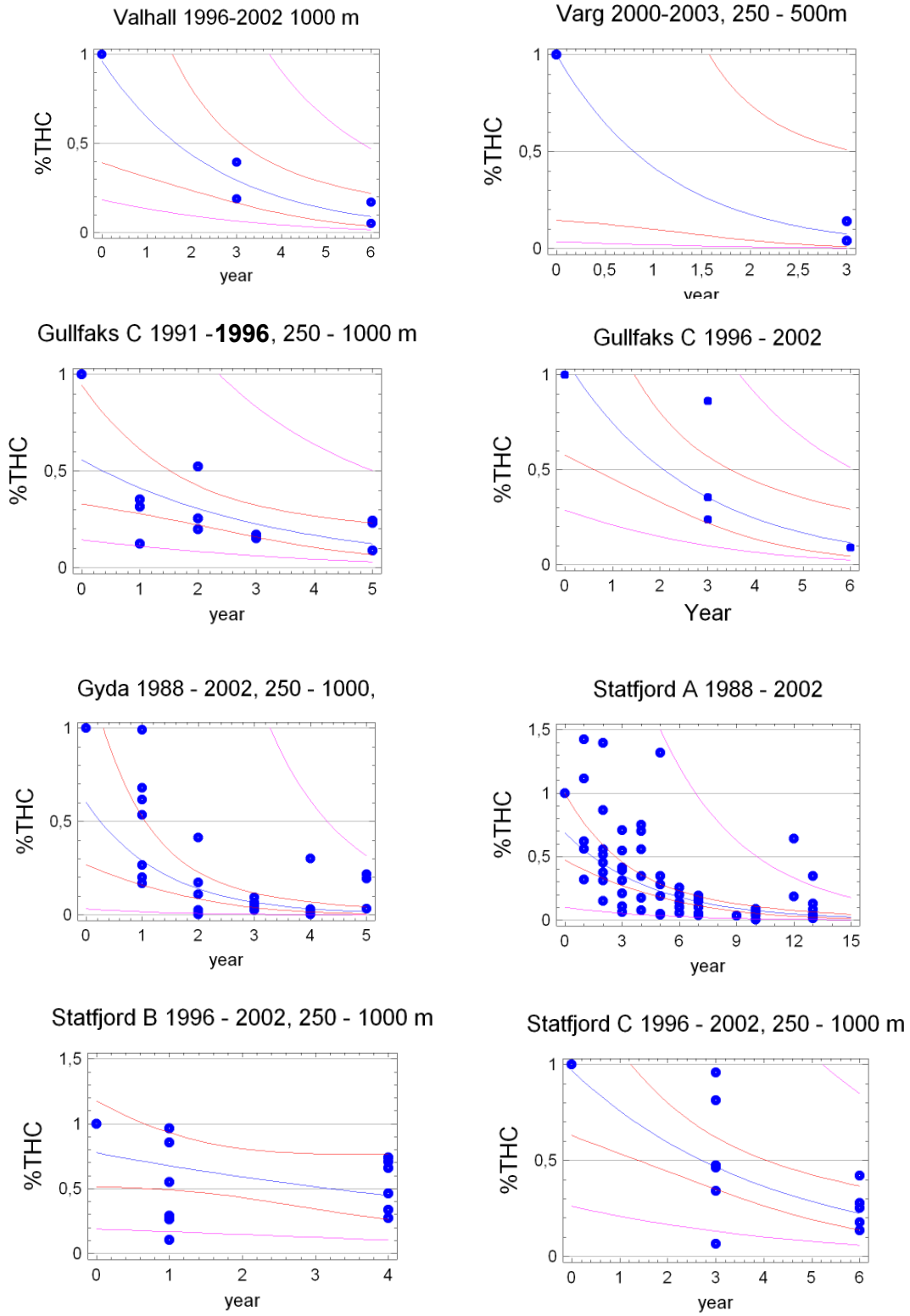


Figure 7. Results of the field specific regression analyses of normalised THC concentrations (relative to year zero) against year since year zero. An exponential model is fitted to the data, showing the regression line (blue), 95 % prediction interval for means of many observations (red lines closest to the regression line), and 95 % prediction interval for new individual observations (outer red lines).

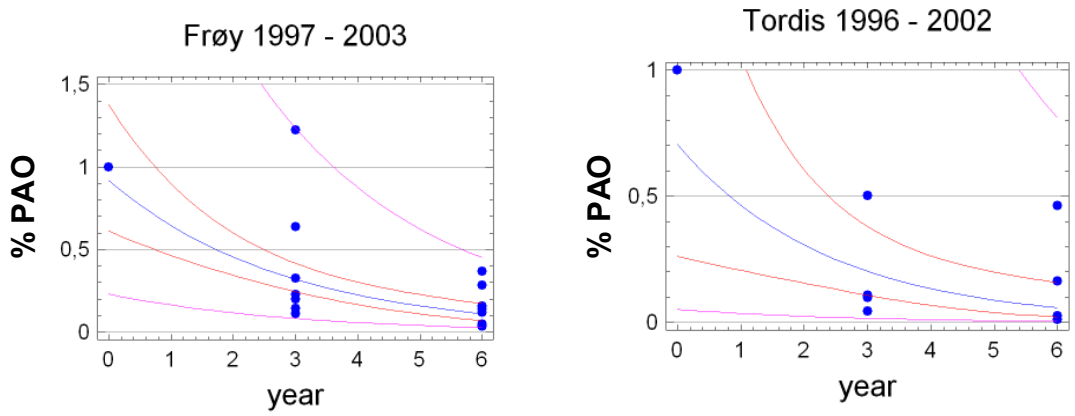


Figure 8. Results of the field specific regression analyses of normalised poly-alpha olefins (PAO) concentrations (relative to year zero) against year since year zero. An exponential model is fitted to the data (Cf. Figure 1 for further explanation).

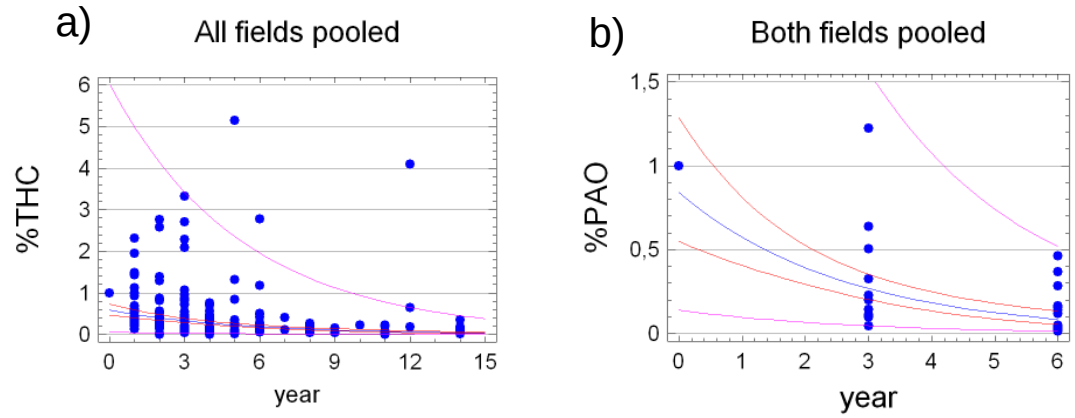


Figure 9. Regression analysis of pooled data for all fields showing degradation of a) THC and b) (PAO). Cf. Figure 1 for further explanation.

The degradation rates estimated from the monitoring data will not reflect true biodegradation in the way one can expect from the experimental data. Offshore fields, and in particular those in shallow water, are subjected to bottom erosion to a greater degree than in the experiments. The result is partly that drilling waste settling to the bottom at one station may be resuspended and transported away, partly that larger cuttings deposits near the discharge site (cuttings piles) may represent a constant input of cuttings to sites further out. The loss rates estimated here must be regarded as a result of biodegradation, import and export of cuttings material due to erosion, and dilution by burial from

natural particle sedimentation. Since these may work both ways it is difficult to predict if the *in situ* loss rates should be higher or lower than the experimentally derived rates.

Nevertheless, the grand mean halflives calculated from field data of 0.8 years for mineral oil and 1.4 years for the PAO (**Table 4**) agreed reasonably well the grand means calculated from the mesocosm experiments of 0.5 years for mineral oil and 0.8 years for the olefin 16-32 (**Figure 1**). A larger larger scatter should be expected for field data than for the experimental data. Neverthelsess, the field data gave generally better curve fits, probably due to the longer time periods of observations of up to 10-15 halflives for field data as compared to one halflife or less in the mesocosm.

It may be important to note that in the experimental work, complete remediation to non-detectable or back-ground concentrations in the sediment has only been obtained for the rapidly degrading esters and olefin C14-C16. Furthermore, not more than 20-80% of the analytical loss of these phases could be accounted for by complete oxidation of organic phase carbon to CO_2. Thus, it is not clear to which extent metabolite formation contributed to the chemical remediation observed neither in experiments nor in the field. Remediation by resuspension and sediment transport could be corrected for by barium normalisation in the experimental work, but the contribution of such processes to the remediation observed in the field is not known.

4. Impact on benthic ecosystem

Various examples of impacts on the benthic ecosystem is given below. The examples are considered to be representative for impacts frequently observed after deposition of drill cuttings deposited on sediments transferred from various fjord locations to the Solbergstrand mesocosm.

4.1 Sediment Oxygen Consumption

Control sediments consumed typically 200-600 µmol O_2 m^{-2} h^{-1}. Sediments treated with cuttings (even the water based, ref. **Figure 3**), showed a consistent increase over control sediments. Maximum rates up to 2000 µmol O_2 m^{-2} h^{-1} frequently occurred 2-8 weeks after addition of cuttings. Subtracting the SOC in control sediments from the SOC in treated sediments yield the "excess SOC" which represent the oxygen consumed by degradation of components present in the added material. Total excess SOC integrated for the entire test periods are shown in **Table 6**. Large intertest variations could to some extent be explained by different dose or layer thickness. E.g. the high excess SOC in the plant oil ester treatments in test 6 obviously resulted from the anomalous high dose added, and the low excess SOC throughout test 10 obviously resulted from anomalous thick layers. Within each test, conditions were more similar with the exception of the intended differences with regard to temperature and community structure in test 9. Test 9 showed that the temperature decrease in combination with the differences in temperature adapted communities had a moderate effect lowering the oxygen consumption during olefin and ester degradation by 30-40%.

The two right-hand columns of **Table 6** show the mean and adjusted mean excess SOC for all tests. The adjusted mean represent our attempt to correct for intended and not intended (systematic errors) inter-test differences. Differences between tests may result from a number of factors. The most important were considered to be:

- natural heterogeneity of test communities (transfer season, sampling location and patchiness at sampling location),
- differences in test set-up and maintenance (box size, stirring rates, flush rates etc.) and
- variations in dose, layer thickness and water temperature.

The mean values were tentatively adjusted to correct for such errors based on the following considerations: Comparisons within tests 4, 5 and 6 gave no rationale to discriminate between mineral oil and olefin 16-32 (test 4), mineral oil and ether (test 5) nor between ether and olefin 20 (test 6). The olefin 16-18 has only been tested once (test 8), and this showed an SOC clearly higher than the SOC for mineral oil. The olefin 14-16 has been frequently observed to consume almost as much O_2 as the esters, but in cases with high dose and layer thickness the difference between the esters and the olefins increased, presumably due to higher availability of esters for anaerobic degradation.

The plot of the adjusted excess SOC vs the degradation constant (**Figure 10**) summarise all results obtained in the mesocosm tests on loss of organic phase in sediment samples and the oxygen consumed during degradation.

Table 6. Sediment oxygen consumption in sediments with drill cuttings added. Values represent the time average for each test period and mean of boxes treated with the same organic phase. The data are corrected for control to yield the excess SOC (µmol O_2 m^{-2} h^{-1}).

Test no.	4	5	6	7	8	9 arctic	9 Oslofj.	10	all tests mean	all tests adj.
Mineral oil	88	336			185			54	166	166
Ether		336	318						327	166
Olefin 16-32	92								92	174
Olefin 20			311	102					207	149
Olefin 16-18					357				357	357
Olefin 14-16				394	306	223	320	58	260	394
Fish oil ester					451	215	360	197	306	451
Plant oil ester	316	672	1205	543	247				596	596

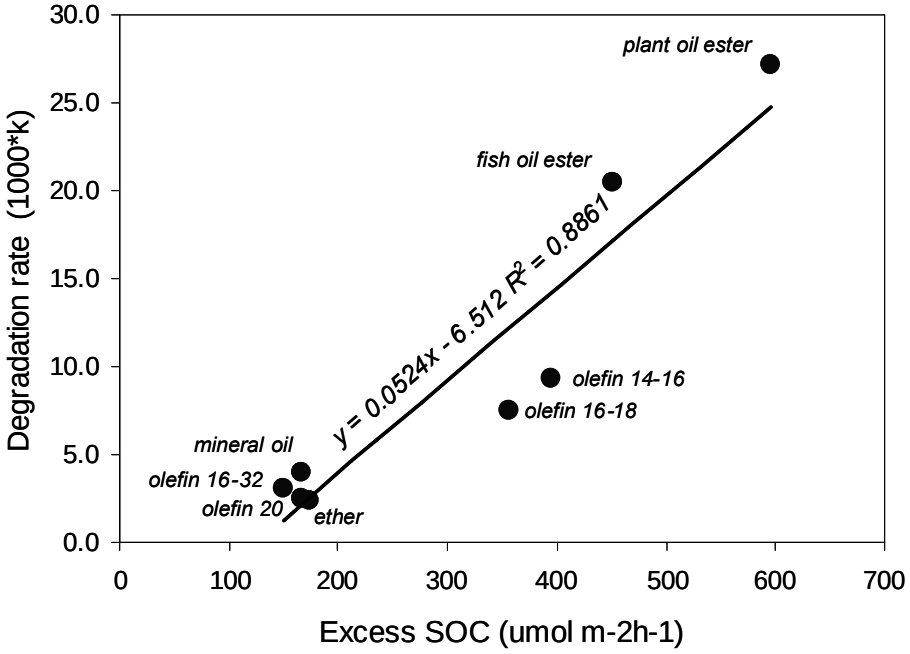


Figure 10. Relationship between degradation constants and "adjusted" (see text) excess cumulative sediment oxygen consumption. Data from **Figure 1**, **Figure 2** and **Table 6**.

4.2 Hydrogen sulphide and redox potential

The activity of sulphide (S^{2-}) ions and redox potentials were measured by direct insertion of metal electrodes into the experimental sediments at various time intervals after addition of cuttings. Typical profiles measured 33 days after addition of cuttings are shown in **Figure 11**, and isoplete diagrams for the whole experimental period are given in **Figure 12**. The isoplete diagrams of the sulphide ion potentials (**Figure 13**) show the presence of free hydrogen sulphide in ester treatments, only. The sulphide event had a maximum occurring just below the cuttings layer 33 days after addition of the cuttings. The sulphide generated by the sulphate reducing bacteria involved in ester degradation is rapidly removed by oxidation and or precipitation as metal sulphides. The redoxpotentials showed, however, that longer time periods are required to restore normal redox conditions. The redoxpotentials also showed maximum effects in the olefin treatments about five months after additon as compared to one month for the ester. Allthough no free hydrogen sulphide was observed in the olefin treatments during test 10, sulphide has been documented in other olefin treaments, but the sulphide production appears to be slow compared to the sulphide production in ester treatments.

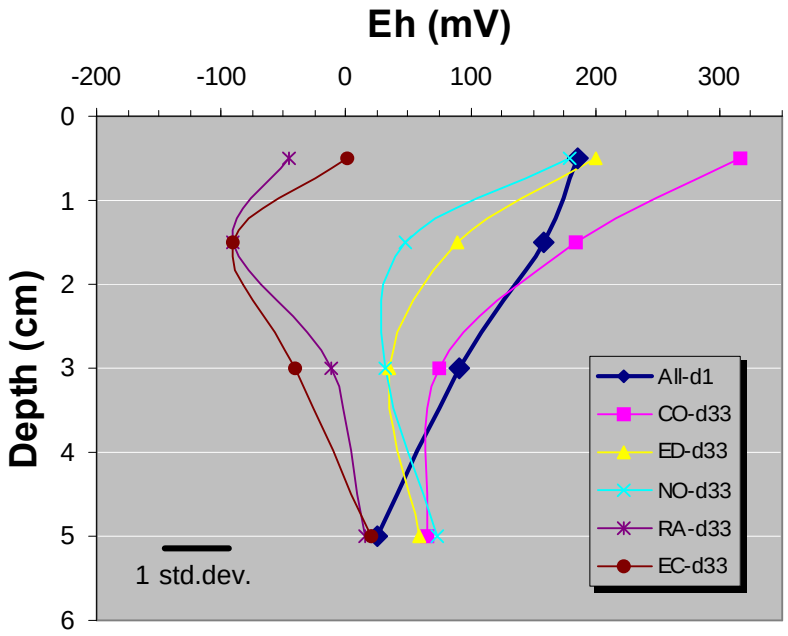


Figure 11. Vertical profiles of redoxpotentials (E_h) in sediments on day 1 (All-d1) and in each treatment on day 33 after addition of drilling muds. All boxes treated with 1 cm frozen sheet containing no mud (CO), mineral oil (ED), olefin 14-16 (NO) and esters (EC and RA). Each point represent mean of three replicate treatments. (Data from test 10).

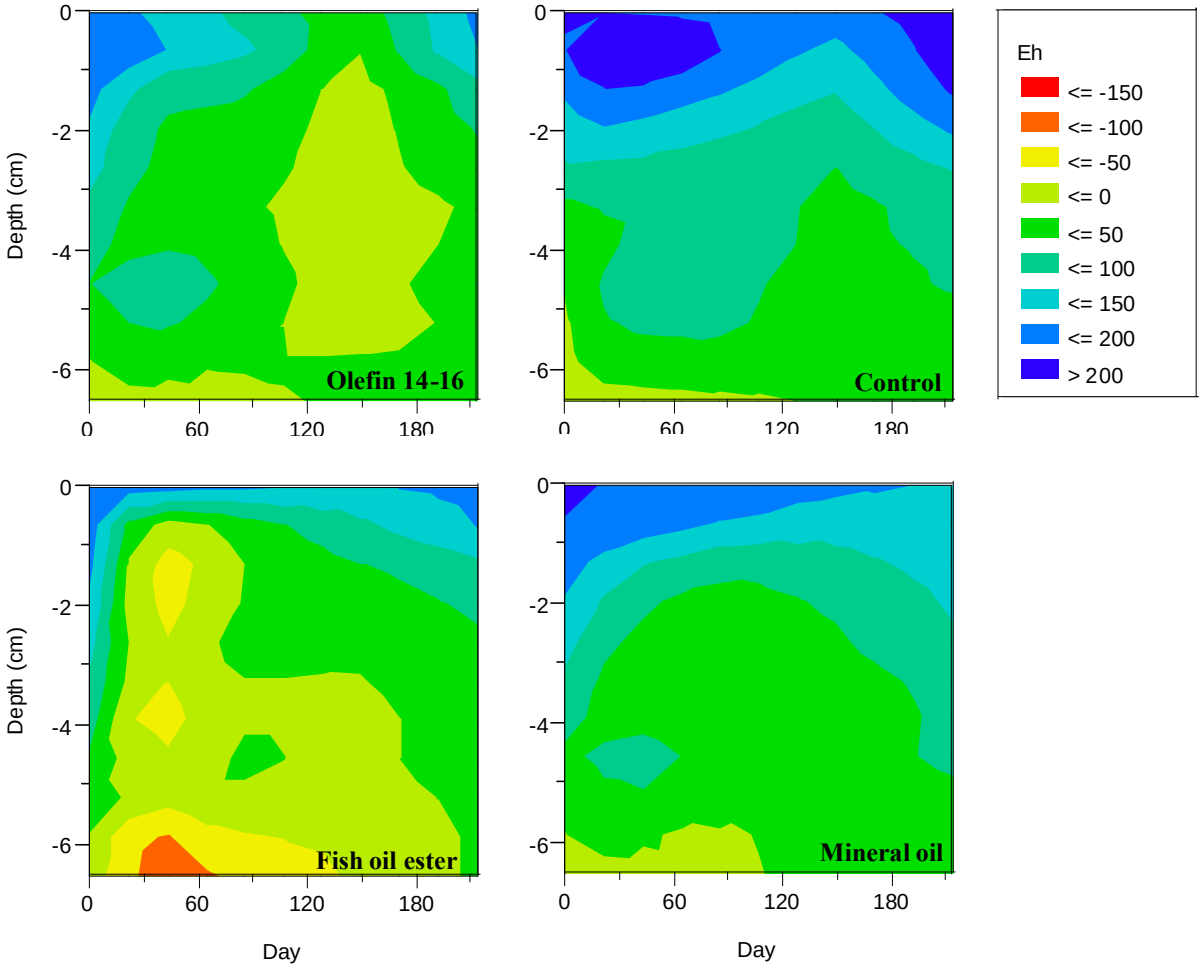


Figure 12. Isoplete diagram of redox potentials (E_h) in the 0-6 cm layer of boxes treated on day 0 with 8 mm frozen sheet of marine clay sediments (control) and marine clay sediments spiked with cuttings to concentrations of 4.6-7.4 mg cm^{-2} of olefin 14-16, fish oil ester or mineral oil.

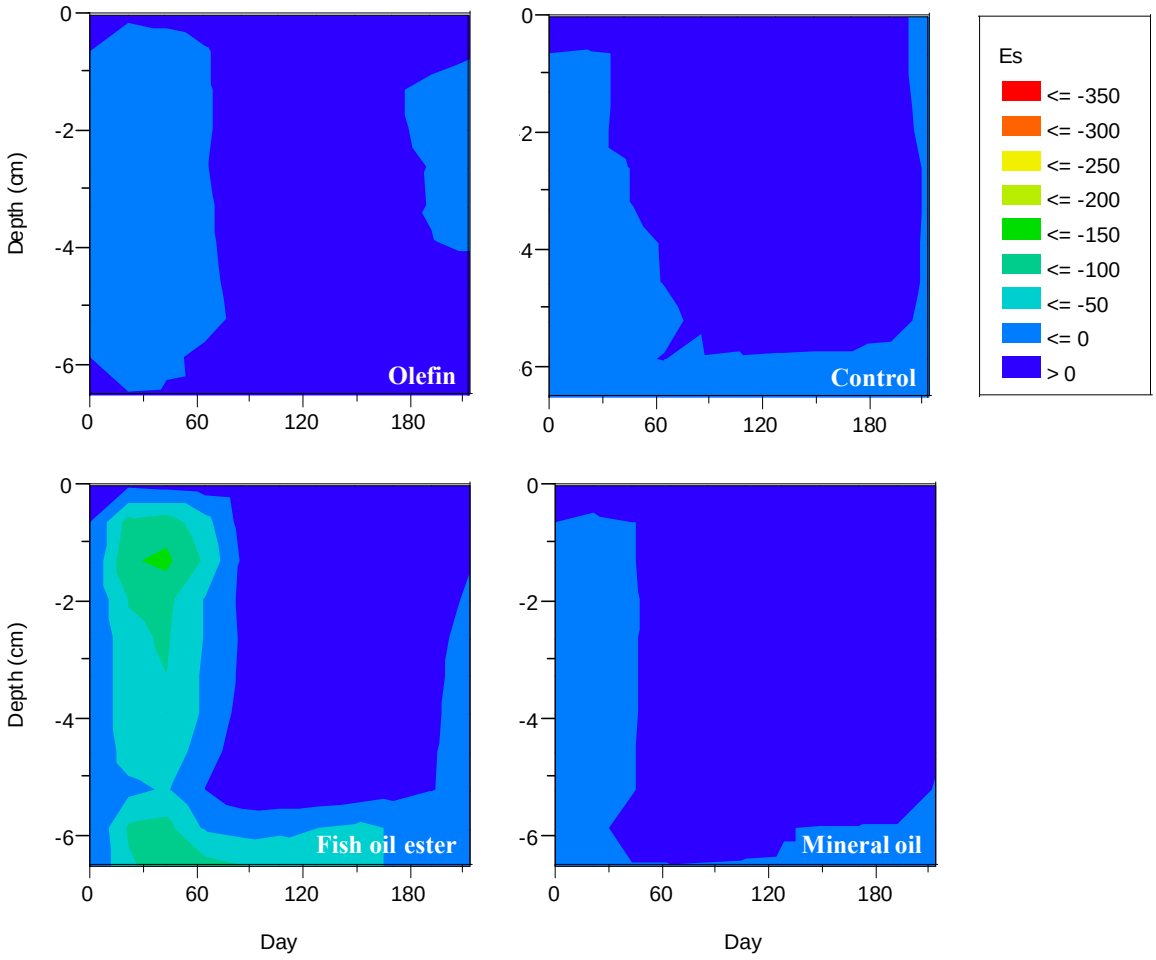


Figure 13. Isoplete diagram of the potentials recorded on a sulphide ion (S^{2-}) selective electrode in the 0-6 cm layer of boxes treated on day 0 with 8 mm frozen sheets of marine clay sediments (control) and marine clay sediments spiked with cuttings to yield concentrations of 4.6-7.4 mg cm^{-2} of olefin 14-16, fish oil ester or mineral oil.

4.3 Macrofauna

Macrofauna analyses performed at the end of each test showed clear effects on sediment communities treated with drill cuttings compared to control sediments treated with corresponding amounts of non-contaminated particles. Data from test 8 (**Table 7**), showed survival of 38 identified species or taxons and 569 individuals in control sediments after six months exposure to experimental conditions. The diversity index was 3.31 corresponding to a class II ("good") environment according to the Norwegian classification system for coastal and fjord sediments (Molvær et al, 1997). Sediments treated with cuttings showed fewer (5-33) species and diversities between 1.4 (class IV, "bad") for the plant oil ester and just above 3.0 (class II, "good") for the olefins. Sediments treated with mineral oil

gave higher diversity, but lower number of surviving species than sediments treated with fish oil ester. Both treatments provided sediments classified as class III "fair" environments.

Prionospio cirrifera was clearly sensitive to any type of contaminated cuttings applied in test 8. The specie has been found to be vulnerable to copper contamination (Olsgaard, 1999, Trannum et al., 2004), but copper is not particularly abundant in the barite based muds applied in test 8. However, in all treatments redox potentials were lowered compared to control sediments, and it appears more likely that the observed decimation of *Prionospio cirrifera* in this experiment was a result of sulphide toxicity or reduced availability of O_2 rather than toxicity of copper.

In general, we have found a correlation between redox potentials and diversity indexes. The effect on redoxpotential tend to precede the effect on the macrobenthic community. This was assumed to explain the moderate effects on diversity observed in test 9 (**Figure 14**) which lasted for three months only. In the Oslofjord sediment, the figure shows primarily redox effects and only from esters. In the arctic sediments, displacement of medium and high dosed sediments towards the lower left of the diagrams showed effects both on redox potentials and diversity, and it could be concluded that the arctic communities were more sensitive to ester and olefin based cuttings, than the Oslofjord communities.

Table 7. Total number of species and individuals (per box), diversity index and number of individuals of each of the most common species or groups of species recovered in the sediments 6 months after addition of cuttings. Mean of two replicate treatments. (Data from test 8).

Species/ Taxon	Control	Olefin C16-C18	Fish oil ester	Olefin C14-C16	Mineral oil	Plant oil ester
Nemertinea indet.	54	33	22	19	23	6
Paramphinome jeffreysi	54	54	43	43	28	42
Prionospia cirrifera	43	1	4	1	1	0
Chaetozone setosa	21	21	13	7	5	0
Heteromastus filiformis	109	290	339	127	143	9
Thyasira equalis	19	49	31	42	22	0
Thyasira obsoleta	8	8	5	9	4	0
Thyasira pygmea	16	46	21	19	12	0
Thyasira sarsi	5	34	29	23	13	1
Number of species	**38**	**33**	**26**	**24**	**19**	**5**
Number of individuals	569	618	546	323	267	57
Shannon-Wiener (H)	**3.31**	**3.01**	**2.26**	**3.02**	**2.51**	**1.39**

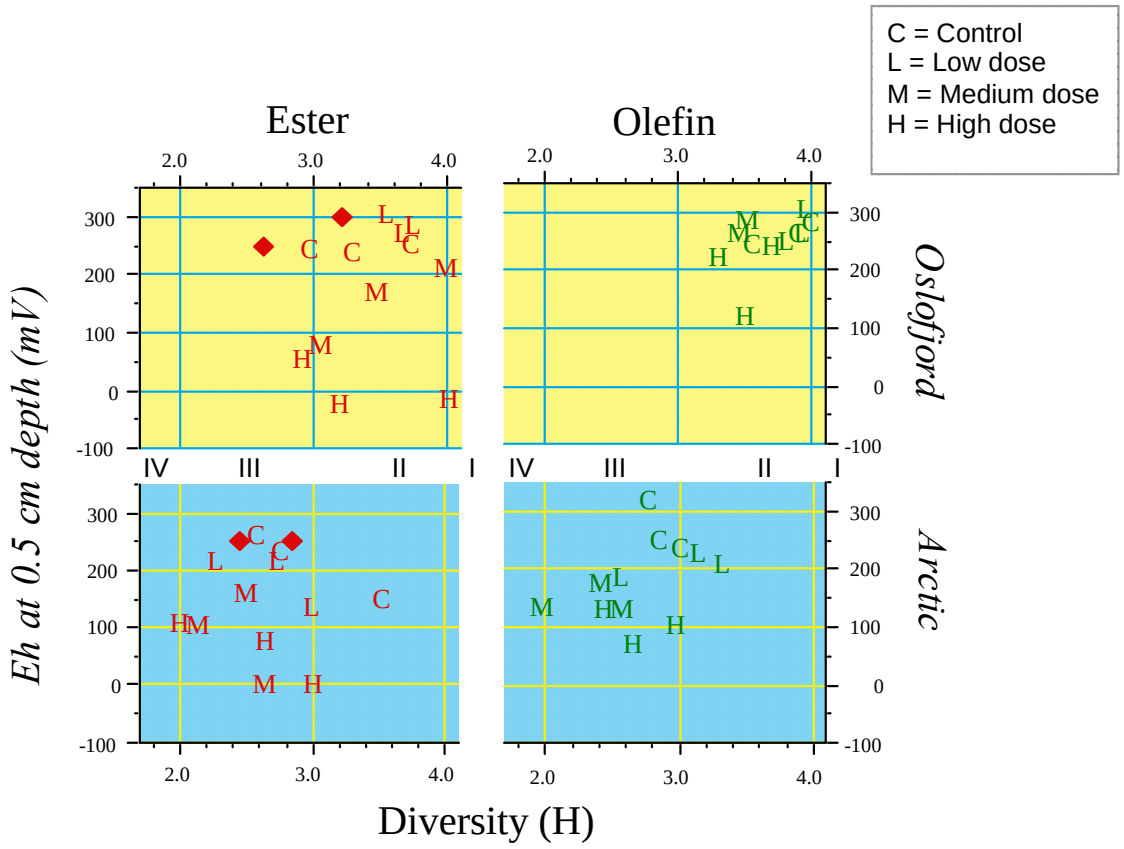


Figure 14. Redox-diversity plots of communities 3 months after transfer to the mesocosm from an Oslofjord and an arctic fjord location and treated with cuttings with fish oil esters and olefin C14-C16 at four different dose levels. Diamonds represent the *in situ* field conditions. (Data from test 9).

4.4 Biological recovery

Data from the mesocosm experiments were not suitable for assessment of recovery. Settling larvae are decimated in the water inlet and experimental periods are relatively short for such purposes. To assess bottom fauna recovery *in situ* we selected three fields, time periods, and stations for which the chemical analyses had shown clear reduction in THC. These were Statfjord B (1996 – 2002, stations 1, 2, 3, 4, 6, and 7), Gullfaks C (1996 – 1999, stations 1, 2, and 3) and Gyda (1993 – 2002, stations 5, 6, 7, 8, 9, 16, and 19). For these we used the Shannon-Wiener diversity index (Hs) as estimator of community recovery. This index was the only common parameter for the selections of fields, periods and stations used. **Figure 15** shows the change in Hs values over time assigning year 0 to be the first year of each time series. The results show that for most of the stations the Hs levelled out after 3 years. Since the resolution of the data material is only 3 years we may conclude that full diversity recovery at a particular station seems to occur within a 3 year period after discharge of oil contaminated cuttings has ceased.

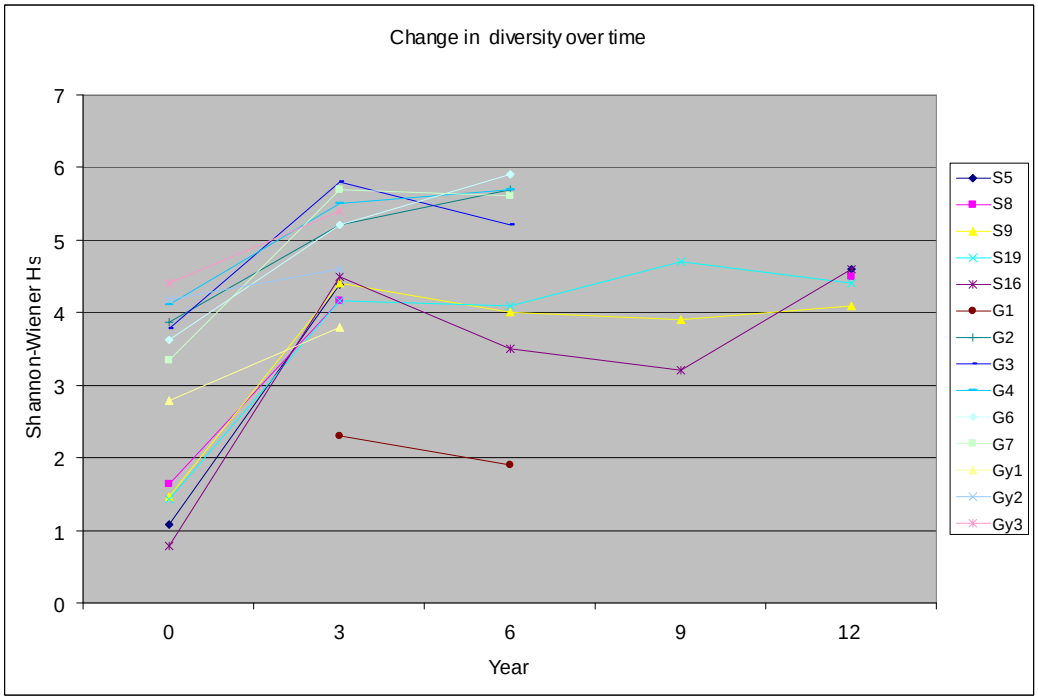


Figure 15. Increase in Shannon-Wiener diversity H of bottom macrofauna with time during periods of clear reduction in THC contamination for a selected set of sediment monitoring stations at Statfjord B (S), Gullfaks C (G), and Gyda (Gy). Numbers in legend refer to station number.

5. Model implications

In accordance with the classical model of Pearson and Rosenberg (1978), the top layer of marine sediments is frequently light grey and penetrated by bioturbating organisms. This layer will have high E_h values, normally within 200 to 400 mV. If the input of organic matter to the sediment is increased, the fauna will be affected due to restricted availability of O_2 and toxicity of H_2S produced by sulphate reducing bacteria. Simultaneously, the colour will tend to become darker due to precipitation of black metal sulphides and the redox potential will decrease to typically -100 to -200 mV. As shown in **Figure 4**, the actual O_2 concentration in a presumably unaffected control sediment is low and the organisms probably depend on physiological adaptations to periodic residence in low-oxic environments and supply of O_2 from the overlying water via siphons, tubes or irrigated burrows. In the ERMS model, the oxygen content of the upper 5 cm layer is assumed to decrease from 100 to 0% saturation due to degradation of the organic phase and negative effects on the benthic community occurs beyond a certain limit value (Rye, mail 06.04.05). We have no data to correlate ecosystem effects with measured concentrations of O_2. Assuming, however, that the O_2-profile modelled in ERMS mimics the redox profile in the sediment as measured on Pt-electrodes, a bridge can be established between the model and our data on effects of the various organic phases on redox potentials and the macrobenthic community.

Test 4-10 encounter 104 experimental units in which the E_h was measured at regular time intervals (often monthly) after addition of cuttings. The measurements were taken 5-15 mm below the sediment surface. The data were normalised to control treatments within each test by:

$$E_h = E_{h,obs}.*E_{h,\text{mean all control}}/E_{h,\text{mean test control.}}$$

and the Shannon-Wiener diversity index (H) was normalised in the same way. The plots of mean and minimum E_h (**Figure 16**) vs H showed significant ($p<0.0001$) decrease of H with decreasing E_h. The group means given in **Table 8** showed that compared with control, both mean and min. E_h was significantly lowered in mineral oil, olefin 14-16 and the two ester treatments (ANOVA, Dunnett's test, $\alpha=0.05$). H was significantly lowered in the two ester treatments, only.

Table 8. Group means of diversity index (H) and mean and minimum E_h (mV) at 5-15 mm depth in sediments 0-7 months after addition of cuttings. n = number of experimental units. * = significantly different from control (ANOVA, Dunnett's test, $\alpha=0.05$).

	Mean E_h	Min. E_h	n(E_h)	H	n(H)
Control	198	161	24	3.36	17
Ether	153	115	4	-	0
Olefin 16-32	156	157	2	-	0
Olefin 20	194	178	3	-	0
Olefin 16-18	137	91	2	3.06	2
Olefin 14-16	130*	85*	27	3.23	22
Mineral oil	120*	71*	8	3.11	5
Fish oil ester	57*	4*	26	2.98*	26
Plant oil ester	33*	-157*	8	1.41*	2

The lowest significant change of E_h occurred in the olefin 14-16 treatments. The difference in mean and min. E_h was 67.8 mV and 80.9 mV, respectively, which corresponded to 41% and 25% of the respective difference between control and the most strongly affected treatment (plant oil ester). If we let the boxes with the lowest mean E_h (-77 mV) and min. E_h (-238 mV) represent the low end of the redox scale, the relative change in the olefin 14-16 treatment was 25% and 20%, respectively. Allthough the diversity was not significantly changed in this treatment the significant relationship between diversity and E_h suggests that fauna-effects should be anticipated at this level of impact.

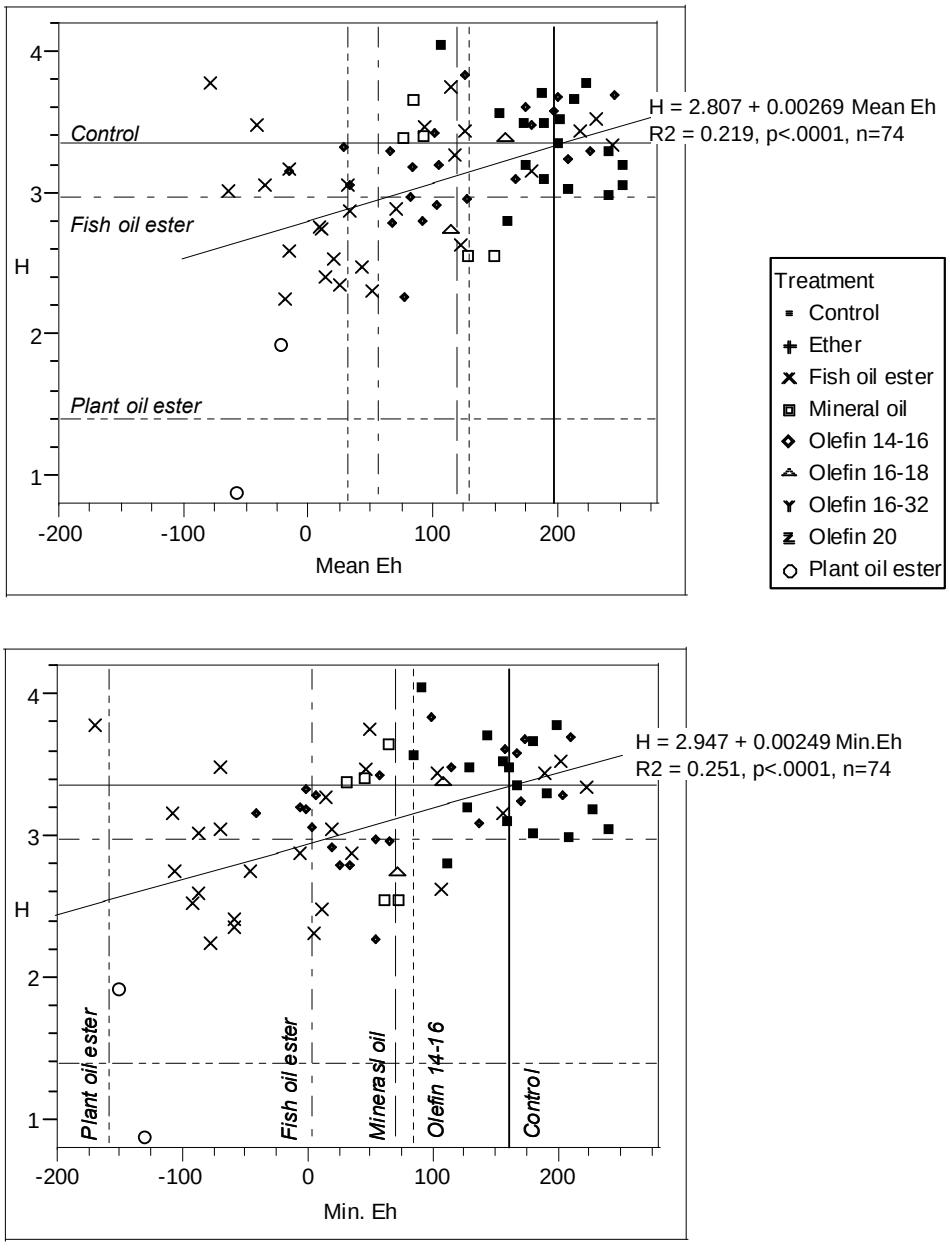


Figure 16. Plots of species diversity (H) vs mean (top) and minimum (bottom) Eh at 5-15 mm depth in sediments 0-7 months after addition of cuttings. Horizontal and vertical lines show all group means significantly different from control. Plotted points and regression analyses on 74 boxes from tests 8, 9 and 10. Group means of E_h in 104 boxes from tests 4-10.

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