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Evaluation of
Overall Marine Impact
of the Novadril
Mud Systems

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Abstract:

The recent increase of discharges of synthetic drilling fluids from offshore drilling operations have caused environmental concern with regard to possible effects on benthic ecosystems. The present report is a review of available data on toxicity, bioaccumulation and biodegradation of the Novadril polya-α-olefin based mud systems as compared to alternative mud systems. Attention was focused on biodegradation and seabed enrichment effects. Thus, in the presence of oxygen, Novadril I and II was found to be biodegradable with half-lifes of 368 and 207 days, respectively. The latter halflife was similar to those of mineral oil, and Aquamul ethers, but longer than the halflife of Petrofree esters. No severe effects have been observed on pH and redox potential in experimental sediments treated with bore hole cuttings contaminated with these muds. From the scarce information available, Novasol III is expected to be a more easily degradable base fluid. No data has yet been made available to assess any change of toxicity and bioaccumulation potential of the modified base fluid.
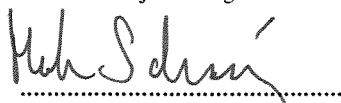
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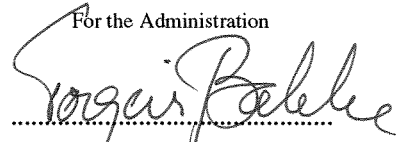2. kjemikalier
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Project manager

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For the Administration

Torgeir Bakke

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Preface

This report has been prepared by NIVA at request from M-I Norge A.S. The report is a review on various information sent forward by M-I Norge A.S. for assessment of environmental effects of the Novadril mud systems. During recent projects NIVA has tested biodegradation of various synthetic drilling fluids in benthic chambers at Marine Research Station Solbergstrand (MRS). Some of the results obtained in these tests have been reviewed and recalculated for the present report.

Oslo, March 20.th, 1995

Morten Thorne Schaanning
Project Manager

SUMMARY

Available information
During the most recent years, NIVA have tested several synthetic muds on cuttings deposited on semi-natural sediment surfaces in benthic chambers at the Marine Research Station at Solbergstrand. In addition to the knowledge on biodegradation and environmental effects derived from these tests, the manufacturer has brought forward results from several tests performed by independent research laboratories as well as results from their own research activities. Much of the latter information appeared, however, rather fragmented, irrelevant and occasionally misleading. Thus, the major conclusions in the present report rests primarily on results from our own tests, standard tests performed by independent research laboratories, and theoretical considerations of the chemical structure of the base fluids.

Chemical structure
The Novasol base fluids are simple straight chain hydrocarbons produced by oligomerisation of α-olefins with eight (C_8H_{16}) or ten $(C_{10}H_{20})$ carbon atoms and a terminal double bond. GC-MS analyses of Novasol I showed predominantly C24 mixed with some C16 and a small contribution of C32 poly-α-olefins. Novasol II, however, proved to be a saturated dimer with the stoichiometric formula $C_{20}H_{42}$. The chemical structure of Novasol III has not yet been confirmed[1].

Bioaccumulation potential
The potential for bioaccumulation is frequently assessed from octanol/water partition coefficients. Because of very high partition coefficients, the potential for bioaccumulation of Novasol has been claimed to be low. The coefficients presented, were however determined from a fluid referred to as AB-5243-SO. Elsewhere in the documentation, this fluid was shown to contain different, longer-chain poly-α-olefins than those predominant in the Novasol base fluids. Nevertheless, an experimental study on bioaccumulation of Novasol and mineral oil in fish showed that uptake of mineral oil was larger than uptake of Novasol olefins.

Toxicity tests
Results brought forward from a number of toxicity tests performed on Novadril I used and unused mud, Novasol II base fluid and Novadril III unused mud, showed EC50 values consistently larger than those required by SFT for moderate toxicity. However, because of the incompatibility with regard to test organisms or test substances, direct comparison of toxicities were not possible, neither between the three Novasol base fluids nor between the three Novadril mud systems.

Aerobic biodegradation tests
The BODIS tests on aerobic biodegradability showed large variations, most of which could probably be ascribed to variations in test procedures. Tests on the three base fluid products performed by Rogalandsforskning, were reasonably consistent showing that Novasol III was slightly more degradable than Novasol II which again was more degradable than Novasol I.

Anaerobic biodegradation

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[1] Recent results from SINTEF Industrial Chemistry appears to confirm that Novasol III is unsaturated and has a shorter chain length than Novasol II (Frøydis Oreld pers.comm.)

In the literature, few enzyme systems are known which are capable to attack unsaturated hydrocarbons in the absence of oxygen (O_2-gas), and degradation of saturated hydrocarbons is thought to be strictly aerobic. Consistent with this knowledge, tests performed by Rogalandsforskning, showed no degradation of Novadril II under anaerobic conditions. Neither did a review of test results reported by TNO, Holland, show any significant anaerobic degradation of Novadril I.

Recently reported 44-49% anaerobic degradation of Novadril III (Rogalandsforskning, 23.11.94) tend to confirm an improved degradability which was to be expected from the molecular composition of the Novasol III base fluid.

Review of NIVA`s benthic chamber experiments
In the benthic chamber studies, half-lives of the base fluids were calculated from exponential regression analyses of the concentration of base fluids in sediments at various time intervals after deposition of contaminated cuttings on replicate sediment surfaces. In spite of considerable scatter, it was concluded that the half-life of 308 days for Novadril I as compared to 207 days for Novadril II was the result of an improved degradability of the Novasol II base fluid.

For Mineral oil and Aquamul ethers, a lag phase of sixty days were assumed to occur before the onset of exponential decrease. The time required for the first halving of the concentration, i.e. the sum of the lag phase and the calculated half-life, was remarkably similar for the fluids attached to Novadril II-, Aquamul- and Mineral oil- cuttings. Also oxygen consumption rates in the chambers treated with these three types of cuttings were very similar throughout the experimental periods. However, differences with regard to lag-phase and respiration ratios between Aquamul and Novadril II might indicate a difference with regard to degradation mechanism. Possibly some of the observed difference resulted from enzymatic cleavage of the ether bond, which might provide a rapid loss of Aquamul ethers without a corresponding consumption of oxygen.

The time-lag between the decrease of concentration of esters and the boom of the oxygen consumption observed in the benthic chambers, was a strong evidence that the mechanism of the natural mineralisation of Petrofree esters was an initial hydrolytic cleavage of the ester bond followed by rapid bio-oxidation to carbon dioxide and water of the organic carbon of the metabolites.

Regression analyses on all data obtained until now on the degradation of Petrofree esters, showed a half-life of 31 days. Regression analyses only on the most recent data gave residence times at about twice this value. Wether this difference was the result of improved test conditions or differences between different cuttings samples is not clear at the moment.

The magnitude and frequency of significant negative deviations of pH and redox potentials in sediments treated with cuttings as compared to control sediments, increased with decreasing half-life and increasing oxygen consumption rates. In spite of up to five times higher initial concentrations of Novasol and Aquamul ethers as compared to Petrofree esters, black, sulphidic sediments were observed in all Petrofree chambers and in none of the others. Thus, for a period of time during and after the discharge of Petrofree cuttings, severe effects on the benthic fauna should be expected to occur at the deposition sites.

Field surveys
Only a few data on concentrations and biological effects of discharged synthetic drilling fluids have yet been obtained from the North sea surveys. Also, the discharge of several types of fluids in the same area, complicates the interpretation of the results from the field surveys. Nevertheless, the results reported so far have been reasonably consistent

with the results obtained in the chamber experiments. Thus, rapid disappearance of Petrofree esters as well as some severe biological effects have been observed at Petrofree discharge sites. Also, a time lag before disappearance of Aquamul ethers as well as much weaker effects on macrobenthic communities have been reported from an Aquamul discharge site.

With regard to Novadril olefins, no field data has yet been reported from the North Sea, but results from the Gulf of Mexico showed that two years after discharge, elevated concentrations of Novasol PAO's were still present in a large area surrounding the discharge site. Slightly increased diversities in the contaminated areas indicated the presence of long-term effects on the community structure. Whether such effects should be allowed or not is a matter of opinion.

Conclusions

1. The Novasol fluids (I, II and III) are synthetic straight chain or slightly branched hydrocrabons, with or without a terminal double bond.
2. Test results demonstrate a relative low toxicity of Novadril I and II muds to marine organisms as might be expected on the basis of their molecular structure and physical/chemical properties.
3. Recent results cited by MI, show similar low toxicity of Novadril III unused mud.
4. Calculated log P_{ow} values for Novasol II and longer chain PAO's, indicate that little or no bioaccumulation should occur with the fluids proper. Neither seabed surveys nor experimental work have provided any evidence of bioaccumulation of Novasol I and II fluids in neither mussels nor fish.
5. Standard BODIS-tests performed at various laboratories have yielded 25-75% degradation of Novasol I, II and III during test periods of 28-157 days.
6. Tests performed by Rogaland Research showed that Novasol III degraded faster than Novasol II, and that Novasol II degraded faster than Novasol I.
7. In the absence of oxygen, degradation of Novadril I and II is still under discussion. Recent results on Novasol III showed a degradation of 44-49% during 69 days.
8. Tests performed under more natural conditions in benthic chambers, showed that Novasol II degraded with a halflife similar to those of Mineral oil and Aquamul ethers. Longer half-lives were found for Novasol I.
9. Effects on pH and redox potentials in sediments contaminated with cuttings containing Novadril I and II were less than the effects of any other drilling fluids tested.
10. Because of the low toxicity and the moderate effects on redox potentials, effects expected to occur on macrobenthic communities in areas contaminated with Novasol I and II should be less than those expected to occur from other drilling fluids tested.
11. So far, the few data reported on seabed effects of synthetic drilling fluids, tend to confirm the results obtained during the benthic chamber studies. This applies in particular to the rapid degradation and major redox effects of the Petrofree esters.

INTRODUCTION

The Novadril mud systems has developed from Novadril I via Novadril II to the most recent Novadril III. The mud system takes their names after the drilling fluids, which have been correspondingly named Novasol I, Novasol II and Novasol III.

Through several tests on cuttings samples deposited on semi-natural sediment surfaces in benthic chambers at the Marine Research Station at Solbergstrand, NIVA has gained some first-hand knowledge on biodegradation and some environmental effects of Novadril I and II as compared to several alternative muds based on ester and ether base fluids. In addition to the knowledge derived from these tests, the manufacturer has brought forward results from several tests performed by independent research laboratories as well as results from their own research activities. Much of the latter information appeared rather fragmented. Thus, the major conclusions in the present report rests primarily on results from our own investigations and standard tests performed by independent research laboratories.

Results of the seabed studies performed on Novadril test sites in the North sea were rather scarce by the time of writing the present report. Thus conclusions are based primarily on experimental work focusing on biodegradation and toxicity.

AVAILABLE DATA

Chemical structure

Olefins or alkenes are straight chain hydrocarbons containing one double bond. If the double bond occurs in the terminal end of the carbon chain, the olefin is called an α-olefin. The Novasol base fluids are poly-α-olefins produced by polymerisation of 1-octene (C_8H_{17}) or 1-decene ($C_{10}H_{21}$). Even though the double-bond may become lost in the production process to yield a saturated hydrocarbon, the poly-α-olefin name may be maintained to reflect its unsaturated origin. A recent practice has been to apply the term "hydrogenated polyalphaolefin" to such products.

The identity of Novasol I and II has been confirmed by GC/MS-analyses at SINTEF-Industrial Chemistry (Oreld and Øfsti, 1993, Oreld, 1994). Thus, the Novasol I drilling fluid was a mixture of oligomers of 1-octene. The most abundant components were the trimer containing 24 C-atoms, followed by the dimer with 16 C-atoms and smaller amounts of the tetramer containing 32 C-atoms. The Novasol II was a hydrogenated dimer of 1-decene ($C_{20}H_{42}$).

According to the information supplied from M-I Norge, the process for making Novasol III is the same as for Novasol II, except for the omitment of the final step of hydrogenation. Thus Novasol III is explicitly claimed to have a double bond and the chemical formulae should be $C_{20}H_{41}$.

Toxicity tests

Results of a number of toxicity tests of Novadril products on marine species are summarised in Table 1. All tests showed EC50 concentrations substantially higher than the limits for moderate toxicity set by SFT or EPA. However, the test results brought forward by MI-Norge to this date encounter different organisms and/or different test substrates (used mud, unused mud, base fluid). Thus, direct comparison of the toxicities of the three Novasol products can hardly be performed. Toxicity of Novasol II base fluid was reported by CMS (Cooperating Marine Scientists) in January 1994, but no results of the toxicity of neither Novasol I or Novasol III base oils have been made available. Unused Novadril III mud tested on the marine algae *Skeletonema costatum* gave EC50 of 5 275 mg kg⁻¹. If compared to the EC50 of 2 100 mg l⁻¹ reported for unused Novadril I mud in 1990, the most recent Novadril mud system appears to have become less toxic to *Skeletonema*. This may result from different mud composition as well as from different toxicity of the base fluid.

Table 1: Summary of test results on toxicity to marine species. Underlined text shows the available sample description, responsible laboratory and date of test performance or report.

Test organism	EC50 (mg l^{-1})	Tox. limit (mg l^{-1})	Comment
<u>Novadril I, unused mud. CMS. 10.09.90.</u>			
Skeletonema costatum	2 100	1 000	Moderate toxicity (SFT-criteria)
Balanus improvisus	69 000	1 000	Moderate toxicity (SFT-criteria)
Mytilus edulis	5	1	Moderate toxicity (SFT-criteria)
<u>Novadril II, used mud. CMS. Jan.1994</u>			
Skeletonema	17 149	1 000	Moderate toxicity (SFT-criteria)
Acartia	>50 000	2 000	Moderate toxicity (SFT-criteria)
Abra Alba	572	20	Moderate toxicity (SFT-criteria)
<u>Novasol II, Base Fluid. CMS. Jan.1994</u>			
Skeletonema	3 905	1 000	Moderate toxicity (SFT-criteria)
Acartia	>200 000	2 000	Moderate toxicity (SFT-criteria)
Abra Alba	628	20	Moderate toxicity (SFT-criteria)
<u>Novasol II, PARCOM ring test. M-I-information 06.01.95</u>			
Corophium sp	>1000		10 day EC50
<u>Novadril III, unused mud. M-I-information, 06.01.95</u>			
Skeletonema	5 275	1 000	Moderate toxicity (SFT-criteria)
Acartia	>37 180	2 000	Moderate toxicity (SFT-criteria)
Abra Alba	798	20	Moderate toxicity (SFT-criteria)
<u>Novadril mud 14.0 ppg. SeaCrest. 96 hr EC50. 3-7. Feb 90.</u>			
Mysidopsis bahia	>200 000	30 000	Moderate tox. (U.S.EPA-criteria)
<u>Novadril mud, 10.0 ppg. SeaCrest. 96 hr EC50. 3-7. Feb 90.</u>			
Mysidopsis bahia	>200 000	30 000	Moderate tox. (U.S.EPA-criteria)
<u>Novasol/Oligomer, 10%. SeaCrest. 96 hr EC50. 3-7. Feb 90.</u>			
Mysidopsis bahia	>480 000	30 000	Moderate tox. (U.S.EPA-criteria)

Bioaccumulation

Calculated octanol/water partition coefficients (log P_{OW}) of the Novasol polyalphaolefins are claimed to be larger than 10.0 (M-I product information, A.J.J.Leutherman, 1990). The ICI Brixham Laboratory estimated logP_{ow} = 14.9-15.7 for a PAO product coded AB-5243-SO. This product was, however, composed of 65% C_{22}, 20% C_{32} and 15% C_{42} and C_{52} oligomers, neither of which were predominant components of the Novasol I and Novasol II base fluids. Measured coefficients of

polyalphaolefins (oligomer composition not specified) exceeded the upper limit of 8.0 which could be determined by the applied HPLC-method.

The bioconcentration factor of most xenobiotics will increase with increasing values of log P_{OW}. However, at very high values of P_{OW}, uptake across biological membranes appears to be inhibited. At log $P_{OW} > 10.0$, the bioconcentration of most substances in most aquatic organisms should be small.

Information on concentration of Novasol PAO´s in animal tissues is rather scarce. A few results of a recent study of fish sampled at a North sea Novadril II well site has been cited in M-I information Jan.1995. Thus, no taste or smell was found in any of the fish sampled. Neither did the concentration of Novasol exceed the detection limit of 0.1 mg.kg-1 in any of the fish samples analysed. No information was given as to where, when and how sampling was performed or how many and which species were analysed. Analyses of commercial fish species captured at the drilling sites is obviously of great public interest. However, because of the lack of control on exposure of the analysed individuals to the test chemical, a field study showing neither smell, taste nor detectable concentrations, yield no evidence that the chemical has a low potential for bioaccumulation.

In an experimental study on uptake of low aromatic mineral oil and Novasol olefins in tissue and gut samples from fish exposed to water equilibrated with contaminated cuttings, Rushing et al, 1991, found detectable amounts of mineral oil components in 32 of the 48 samples analysed. Olefins were, however, only found in one gut sample and none of the samples of fish tissue. Both mineral oil and olefins were shown present in the water of the aquaria throughout the 32 days period of exposure. They concluded that the contrast between the mineral oil and the polyalphaolefins was a result of restricted uptake of the larger olefin molecules across gill and digestive structures.

Biodegradation

Aerobic tests on biodegradation

Aerobic biodegradation is most commonly determined by the standard laboratory bench test BODIS 28. The test substance is added to a standard substrate and oxygen consumption is measured over 28 days. For slowly degrading substances the test may be prolonged until oxygen consumption approaches zero. The results of aerobic degradation tests performed by several laboratories on various Novasol products is shown in Table 2 and Figure 1.

The % degradation of Novasol I in a test performed by Rogaland Research in 1991 was calculated using two different procedures for the determination of COD (Chemical Oxygen Demand). The higher value was calculated from a procedure which gave a COD of 0.99 mgO2/mg sample. The lower values was calculated from a COD of 2.81 $mgO_2 \cdot mg^{-1}$ sample, determined by a modified Kelkenberg method using a more powerful oxidation procedure. The latter value was more close to the ThOD (Theoretical Oxygen Demand) of 3.43 $mgO_2 \cdot mg^{-1}$ PAO. The lower values were reasonably consistent with other laboratory tests cited in the M-I information package.

Table 2: Results of laboratory bench tests of aerobic biodegradability of various Novasol products.

Test protocol	Test substance	Days	% deg.	Reference
BODIS-28	Novasol III	28	48	RF-278/94, 17.11.94
		57	57	
		116	75	
BODIS-28	Novasol II	28	41	RF-266/94, 15.11.94
		59	53	
		112	56	
		157	57	
BODIS-test	Novasol I	28	14 (39)	RF, 25.01.91,[2]
		45	18 (52)	
		60	22 (63)	
		83	25 (72)	
BODIS-Sea Water	Novasol II	28	70	TNO report IMW-R 93/120
Mod. Sturm	AB-5243-SO	28	28-29	LSR Report 90/MGB001/0584

Thus, rejecting the higher values for Novasol I, the test data from Rogaland Research (Figure 1) might seem to confirm the improvement of degradability from Novasol I via Novasol II to Novasol III.

The 28 days degradation of Novasol II of 70% was obtained at TNO using a natural sea-water incubation medium. This test showed a high rate of degradation as compared to the other test results. The different incubation media may explain the different test results on Novasol II obtained by the different laboratories.

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[2]Numbers in brackets calculated relative to COD measured by NS4748. RF showed that the organic carbon in the drilling fluid was far from completely oxidised by this method.
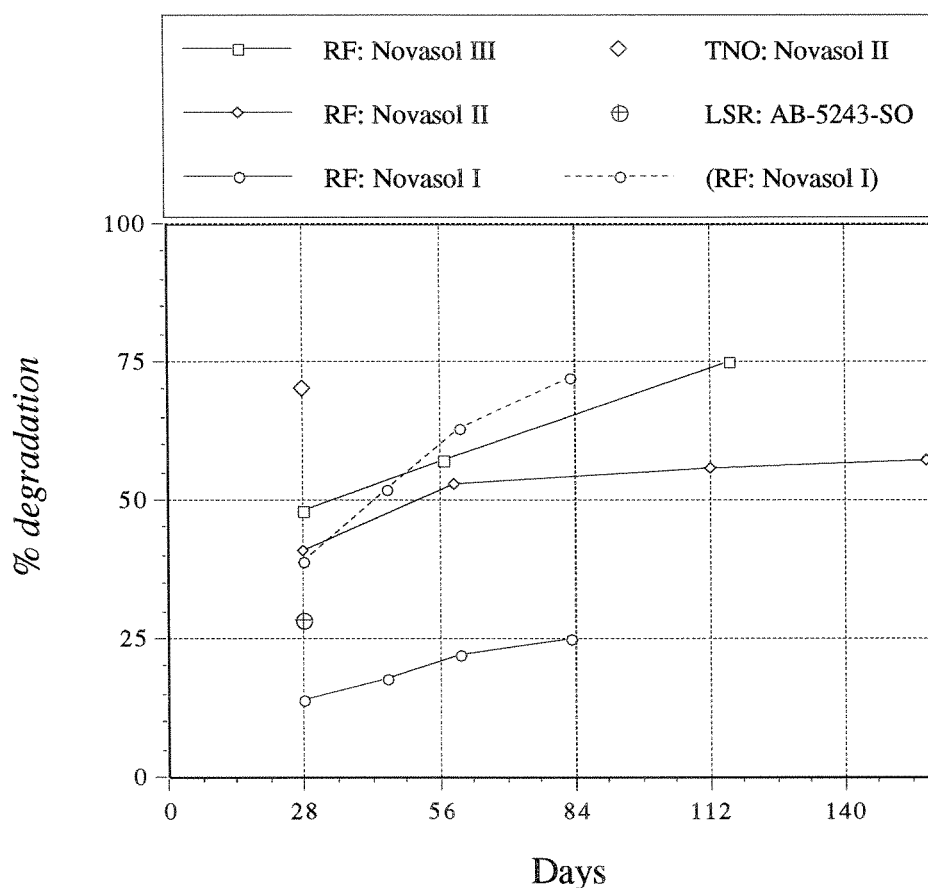
Figure 1: Results of various tests on aerobic degradation of various Novasol products.

Anaerobic tests on biodegradation

The metabolism of saturated hydrocarbons as well as many branched-chain unsaturated hydrocarbons is thought to be strictly aerobic (Schink, 1988). This conclusion is supported by experimental work as well as the stability of such compounds in old anoxic sediments. Thus, the anaerobic degradability of the Novasol I and hydrogenated Novasol II products found by TNO appeared controversial, and was not consistent with the results reported by Rogaland Research (Table 3).

The only well documented study of anaerobic degradation was the degradation of Novadril I (TNO report R 92/069). In this study, aliquots of Novadril mud was incubated with anaerobic sludge at 35°C. Gas produced in the bottles was measured at regular intervals over the test period and compared with gas produced in control bottles containing only anaerobic sludge. From the excess cumulated gas production in treated versus control bottles, the % degradation of Novasol carbon was calculated. It appears obvious that if the gas production in the bottles containing the test sample was not significantly different from the gas production in the control samples, it is not possible to claim that a degradation of the test sample has occurred. No such calculation was performed in the TNO-report, and two of the six control bottles were rejected before calculation of the biodegradation.

Table 3:Results of laboratory bench testing of anaerobic biodegradability of various Novasol products.

Test protocol	Test substance	Duration (days)	% degradation	Reference
ISO CD 11734	Novadril III	69	44-49	RF-288/94, 23.11.94
ISO CD 11734	Novadril II	38	-30	RF-prelim. results
		21	-24	RF-prelim. results[3]
	Novasol II base fluid	140	40-46	TNO, prelim. results
ISO/DIS 11734	Novasol II base fluid	183	26	TNO, prelim. results
ISO/DIS 11734	Novadril I	133	53-106	TNO-report R 92/069

Table 4: Cumulative gas volumes in ml per bottle calculated from table B1 in TNO report R 92/069 and statistical significance of the observed differences.

Series	A	B	C	D	E	F
Bottle numbers	1-3	7-9	50.1-50.3	4-6	10-12	50.4-50.6
Par. 1	21.6	23.6	21.7	15.0	16.9	17.4
Par. 2	23.8	23.4	23.7	18.0	15.7	18.1
Par. 3	23.3	23.3	24.9	16.9*	15.8	19.6
Average	22.90	23.43	23.43	16.63	16.13	18.37
Std. dev.	1.15	.15	1.62	1.52	0.67	1.12
Mean difference	.53	.00	-	1.73	2.23	-
Significant 95%	no	no	-	no	no	-
Significant 90%	no	no	-	no	yes	-

*Four missing values of gas volumes in control bottle no 6 (day 77, 91, 107 and 133) were replaced with the mean gas volumes measured in bottles nos. 4, 5, 10, 11 and 12.

Table 4 shows the sum of the gas volumes determined at 13 occasions during the 133 days study. Bottles 50.1 to 50.6 contained 4.2-5.9 mg test substance in a sludge volume of 94.4-94.6 ml. Bottles 1-12 were control samples containing 94.1-94.6 ml sludge, only. After eight weeks, a polyethylene glycol reference substance (PEG 400) was added to the bottles in series A, B and C. Rapid degradation of the standard yielded an extra gas production of 5-7 ml in these bottles.

Statistical analyses of the variance (ANOVA) of the A-C series of spiked samples revealed no significant difference between between the Novadril bottles (C) and control series (A and B). In the non-spiked bottles, the volumes of gas produced in the Novadril bottles (F) were not significantly different from control series D (p>0.1), and the p-value of .09 against series E was neither very convincing.

TNO´s conclusion of a degradation between 53 and 106% was drawn after rejection of the control bottles which gave the lowest gas production. In our opinion, the only possible conclusion which can be drawn from this test, which was very well

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[3]By 06.01.95, test has been running for another 50 days without any degradation.

documented and appeared to be thoroughly performed, was that no significant degradation of the Novadril olefins had occurred during the experimental period.

Benthic chamber studies

Experimental outline

The results obtained during three benthic chamber experiments performed at Solbergstrand Marine Research Station during the period 1992-1994 has been reviewed for cross-test assessments. Because of different assumptions and data treatment, as well as reanalyses of the Aquamul ether samples from test 3, the present results may be slightly different from the results derived in the original reports.

Test set-up and sampling techniques were considerably modified between the first test on Novadril I, and the subsequent tests on Aquamul and Novadril II. Thus, comparison of the results obtained in test 1 with those obtained in tests 2 or 3 may be less reliable than comparison of results obtained in tests 2 and 3.

Thin layers of cuttings were mixed into the overlying water and allowed to settle on top of sediments kept in replicate 0.25-0.5 m^2 chambers. In addition to the test objects, chambers treated with Mineral oil, Petrofree ester and Aquamul ether cuttings were used for reference and chambers not treated with any cuttings were used for control.

Analyses

At various time intervals during experimental periods of 148-212 days, pH and redox potentials were measured *in situ.* within the 0-3 cm depth interval. Sediment samples were collected for GC-analyses of Novasol olefins, Aquamul ethers, Petrofree esters and Mineral oil THC. Sediment oxygen consumption was measured bi-weekly in treated and control chambers.

Results

All results of the chemical analyses are shown in Figure 2. Results of the respiration measurements are shown in Figure 3 and results of the pH and redox potential deviations from control sediments are shown in Figure 4. Mean results calculated for each of the drilling fluids are summarised in Table 5.

Probably because of a sampling error during sampling of recently deposited drilling fluids, concentrations were occasionally found to increase during the first two months of the experiment. Therefore, the highest average concentration observed in each chamber during the 0-62 days period, rather than the concentrations determined 2-3
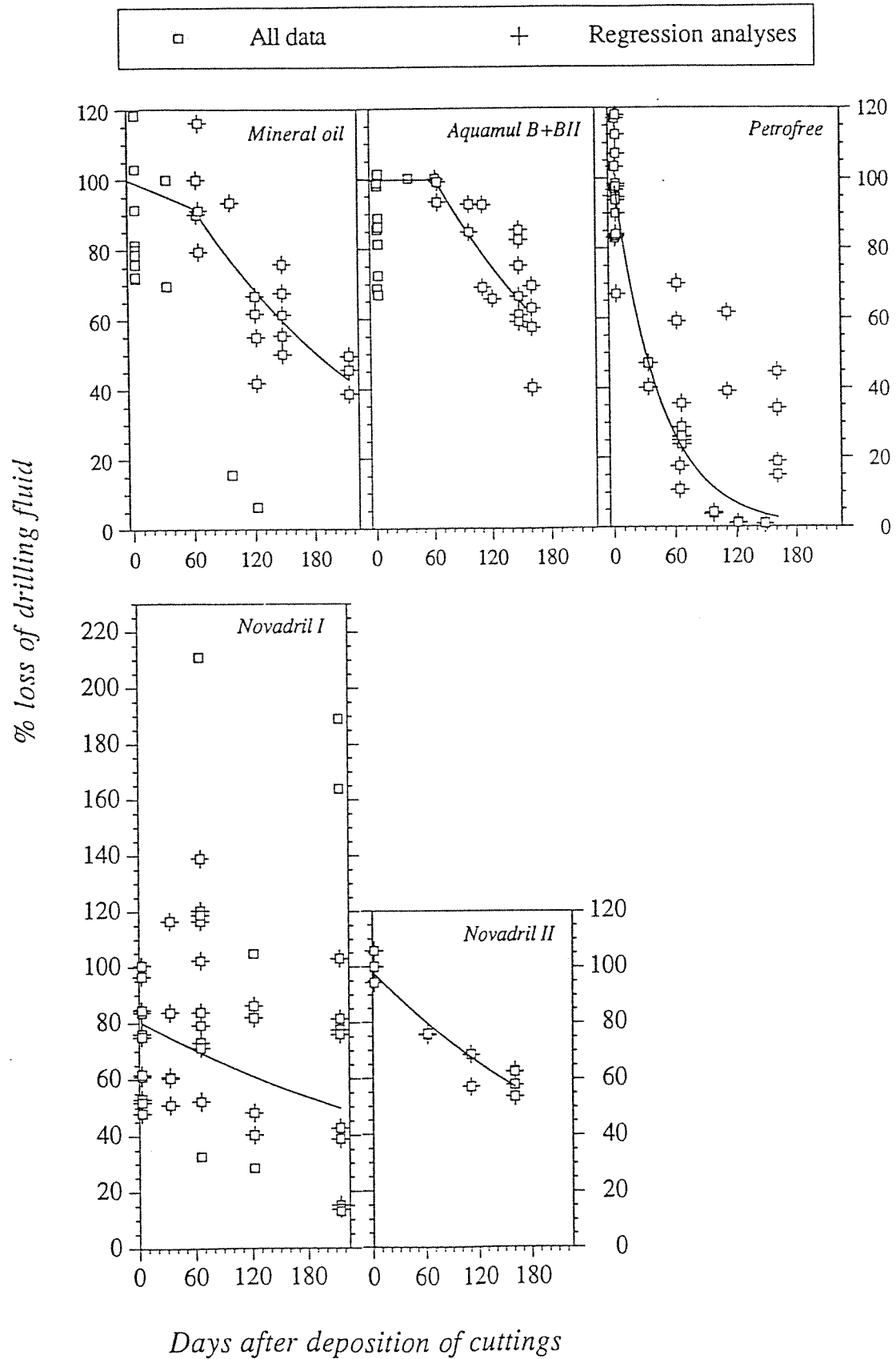
Figure 2: Normalised concentrations of drilling fluids in benthic chamber sediments at various time intervals after deposition of cuttings. Superimposed crosses highlights the data used for exponential regression analyses. Regression curves are shown as curved lines. Calculated correlation coefficients and half-lives are shown in Table 5.

Table 5: Summary of results of benthic chamber tests (see text).

Test substance	Initial conc. µg·cm⁻²	Total loss % of initial	Resp. ratio % of loss	Lag phase days	Half-life days	Coeffi-cient r	Effects (ΔEh) mV
Novadril I	3.2-15.1	55[1]	22	60	308[1]	.370[2]	53
Aquamul	13.3-17.9	38	21	60	140	.764	71
Novadril II	6.3-9.9	43	37	0	207	.951	55
Mineral oil	3.2-5.3	57	59	60	139	.816[3]	79
Petrofree	3.5-17.2	95	39	0	31	.774	268

[1]Highly uncertain   [2]Omitted 4 high and 4 low values   [3]Omitted 2 low values

days after each treatment, were taken to represent the initial concentration (=100% level in Figure 2).

Neither mineral oil, nor Aquamul showed any decrease during the first two months. Thus, as shown in Table 5, lag phases of 60 days were assumed for these fluids.

Furthermore, two extraordinary low values were omitted from the mineral oil data. The large scatter of the Novadril I concentration data was reduced by omitting the highest and lowest values from each of the data sets obtained after day 60. Assuming loss to be dependent only on the concentration of the drilling fluid, curves were fitted by exponential regression analyses on the remaining data. Regression curves are shown in Figure 2, and regression coefficients and half-lives calculated from the curve equations, are given in Table 5.

The excess sediment oxygen consumption rates shown in Figure 3, were calculated by subtraction of the rates measured bi-weekly in control chambers from the corresponding rates measured in the treated chambers. Before plotting, the data were smoothed using a three channel binomial function.

The total loss of drilling fluids given in Table 5, were taken from the plots in Figure 2. The loss by respiration was calculated from the excess oxygen consumption accumulated during the entire experimental periods and converted to carbon equivalents using the theoretical oxygen demand (ThOD) of the respective drilling fluid. Thus, the values in the fourth column of Table 5, shows the fraction of the total loss which had been converted to carbon dioxide.

On each sampling occasion, pH and redox potentials were determined at three depths at three different locations in each chamber. The negative deviation for each chamber and treatment was calculated by subtracting the mean value in control sediments from the mean value at the corresponding depth in the treated chambers. The average deviation for the three depths were plotted in Figure 4. The effect on the redox potential summarised in the last column of Table 5, represents the average of the maximum deviations found in each test and treatment. Thus each of the E_h-deviations given in Table 5 represents mean values of 6-39 single determinations of E_h.

Figure 4 shows that both pH and E_h within the top 3 cm of the sediments decreased after deposition of the cuttings. The decrease of the pH is a result of the enhanced production of CO_2 during aerobic decomposition of the fluids. During sulphate reduction pH is

buffered by the simultaneous release of hydrogen sulphide. Thus, pH was not particularly low during the sulphide events in the Petrofree chambers.

Relatively large positive deviations were observed during the initial surveys of the Aquamul chambers. These high values revealed the presence of alkaline mineral buffers, which are common additives in many mud recipes.

It should be noted that with regard to commonly used limits for biological effects, the pH deviations observed throughout the test chambers, were small. The zero values in Figure 4 were about 7.8-7.9. Thus the range of the mean values were 7.3-8.7. The lower values were similar to those frequently found in natural, slightly enriched sediments. The high initial pH values observed in the Aquamul chambers were, however, beyond the natural range of pH in marine sediments.

Throughout most of the experimental periods, redox potentials were 0-100 mV lower than the potentials observed in non-treated control chambers. This moderate lowering of E_h shows enhanced metabolic decomposition processes within the sediment surface. In all chambers treated with Petrofree esters, the redox potential deviations dropped to 200 mV and more. The shift towards the extremely low values occurred at about day 60, and always immediately after the boom of the oxygen consumption rates. However, in the low dose Petrofree chambers (test 1 and 2) the redox potentials increased to small negative deviations shortly after the decrease of the oxygen consumption rates. In the high dose chambers in test 3, neither oxygen consumption rates nor redox potentials were observed to normalise within the experimental period.

As confirmed by the appearance of black areas and white mats of sulphide oxidising bacteria on the sediment surface, as well as the characteristic smell of hydrogen sulphide from the sediment samples, the extremely low redox potentials were obviously controlled by the presence of hydrogen sulphide in the pore water. Such sulphide events are known to give dramatic effects on the structure of benthic communities. No systematic work on the community structure was done in the present tests, but several individuals of brittle stars were observed to perish on the sediment surface during the sulphide events in the Petrofree chambers.

Suitability of parameters with regard to seabed remediation

Because of the highly specific GC-analyses of synthetic drilling fluids, initial enzymatic reactions such as the hydrolytic cleavage of ester-bonds, may provide high rates of loss of the mother compound. However, the pool of hydrocarbons may remain nearly unchanged in the environment in the form of metabolites which will not show up in the GC-analyses. These metabolites may behave different than their mother compounds with regard to water solubility, bioaccumulation, toxicity and biodegradability. If substantial amounts of metabolites are produced, total loss of synthetic drilling fluids as a measure on seabed remediation might be rather misleading.

The limitation does not apply to the rates derived from oxygen consumption measurements. The respiratory loss, is a measure on the ultimate oxidation of drilling fluids to CO_2 and water. It may be thought of as a measure on the dissipation of the chemical energy added to the system by the initial sedimentation of drilling fluids. Not until the entire degradable fraction of drilling fluids, metabolite compounds and carbon
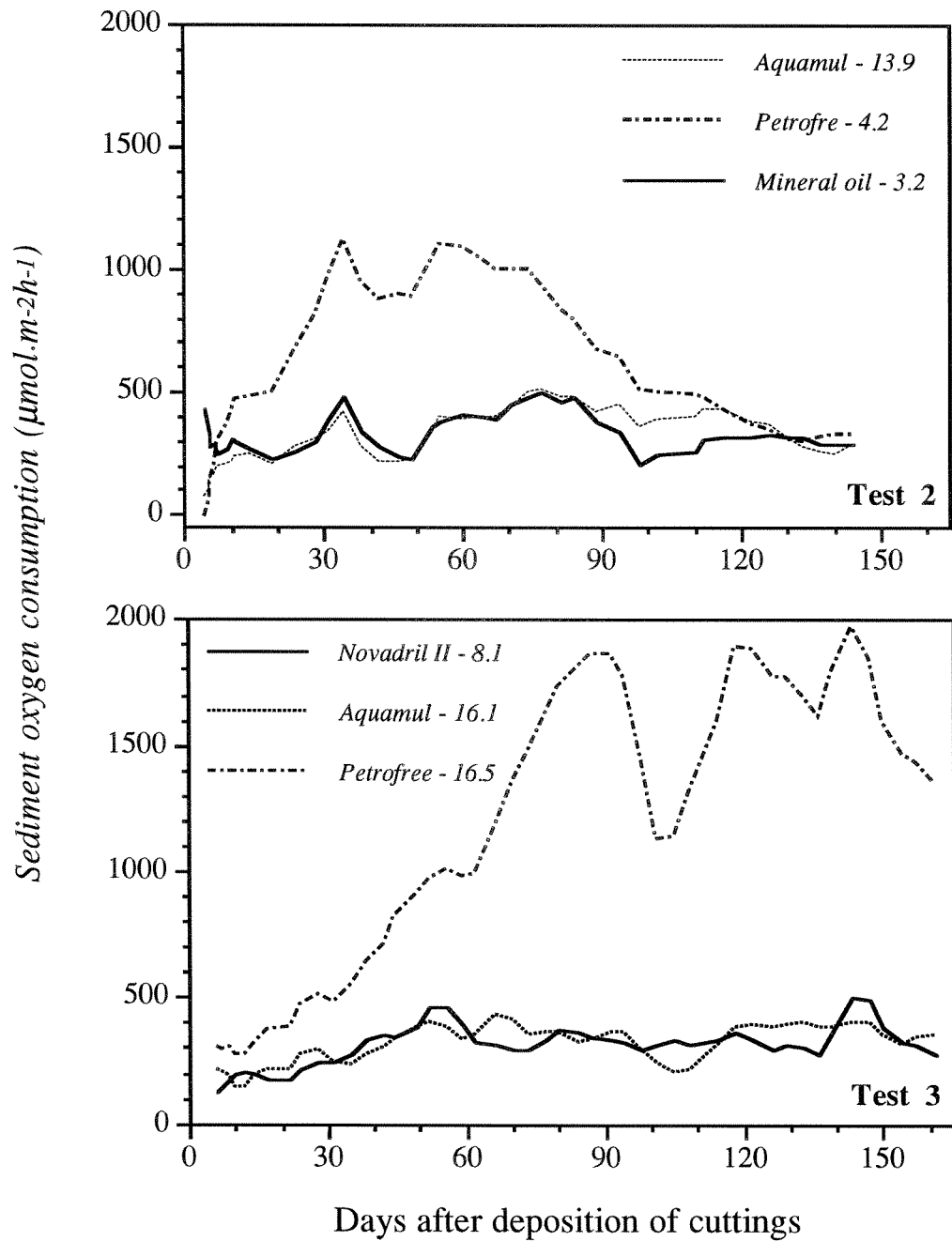
Figure 3: Excess oxygen consumption in treated chambers. Initial concentrations (μgDF·cm^{-2}) are given in legend.
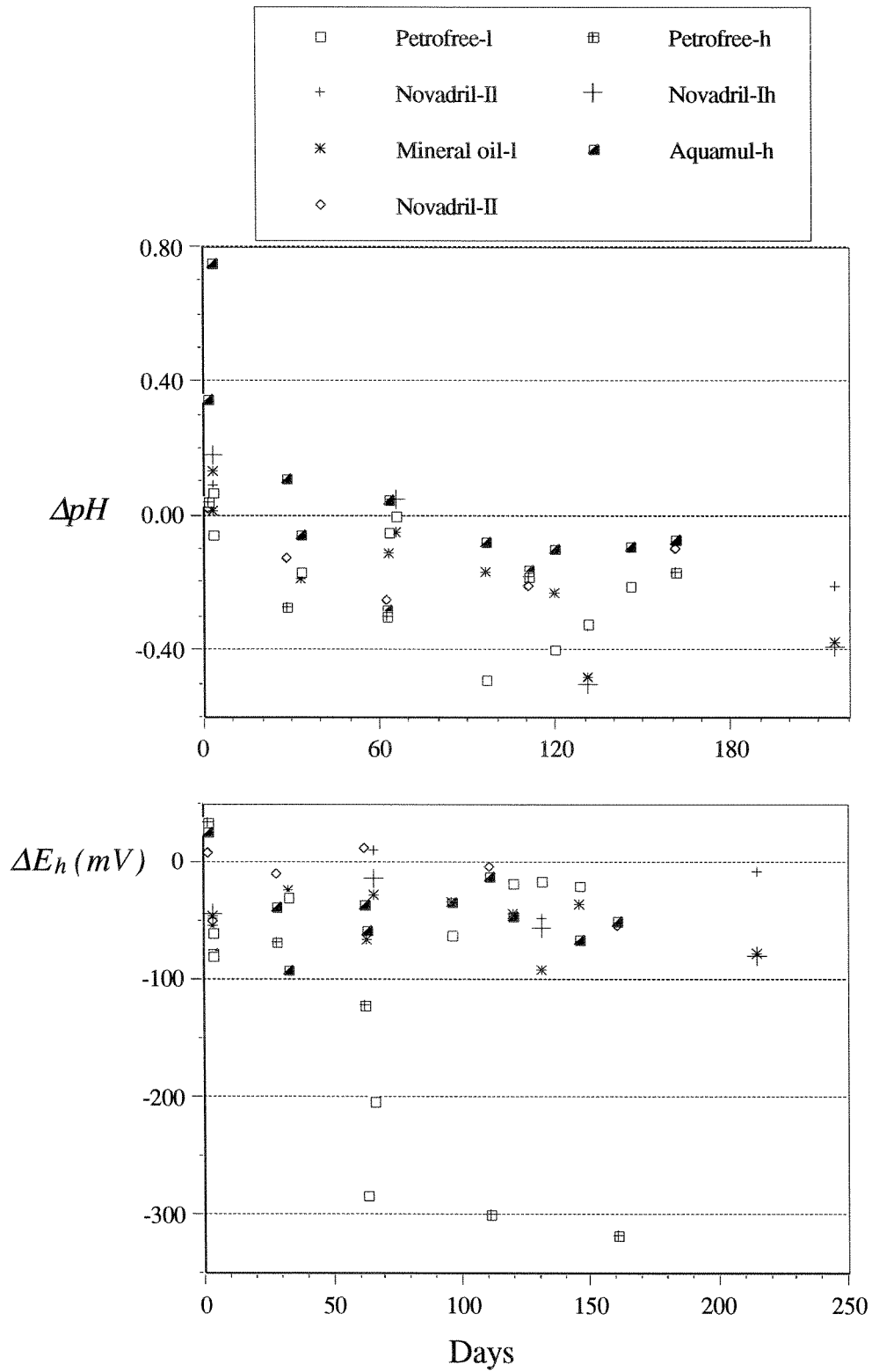
Figure 4: Effects on pH and redox potentials.

assimilated in the decomposer community has been converted to CO_2 and water, and reduced compounds have been reoxidised or entered stable mineral fractions, the oxygen consumption will return to predeposition levels and seabed remediation may be considered complete. Inert organic and inorganic fractions originating in the cuttings material may still be present in the sediments, but the environmental effects of such compounds will probably be negligible.

Comparison of the various drilling fluids

The average loss of mineral oil of 57% (Table 5) was somewhat higher than the 38% loss of Novadril II and 43% loss of Aquamul. Because, however, improved oxygen availability in the cuttings layer will favour biodegradation in low dosed chambers, these differences may be artefacts of the different ranges of initial concentrations. Considering also the similarity of the sum of the lag phase and half-life ranging from 199 days for the Mineral oil THC via 200 days for the Aquamul ethers to 207 days for the Novadril II olefins, the tests gave no evidence for claiming any difference with regard to total loss rates of those fluids.

The respiration data obtained in test 1, before modification of the test set-up, could not be directly compared to the data obtained in tests 2 and 3. However, the mean respiration rates of 223 and 272 $\mu molO_2 \cdot m^{-2} h^{-1}$ in the low and high dose Novadril I chambers, respectively, was not much different from the mean respiration of 243 $\mu molO_2 \cdot m^{-2} h^{-1}$ in the low dose Mineral oil chamber. Figure 3 shows that throughout the experimental periods, the respiration rates of Mineral oil and Aquamul ethers during test 2, as well as those of the Aquamul ethers and Novadril II olefins during test 3, were very similar.

Thus, neither drilling fluid analyses nor sediment oxygen consumption measurements revealed any significant differences in rates of biodegradation between Novadril II, Aquamul ether and Mineral oil.

Petrofree esters, on the other hand, were more or less completely lost during the experimental periods. The half-life of 31 days was less than 1/4 of the half-lives of the other fluids. Respiration rates were high and dose dependent (Figure 3).

However, as shown in Figure 4 and in the last column of Table 5, the negative redox deviation was much more severe than the moderate lowering observed to result from the other fluids. This is the cost of using a highly degradable drilling fluid.

Unaccounted loss

Several factors, such as

- loss of drilling fluids attached to particles via processes such as bioturbation and resuspension,
- loss of dissolved drilling fluids to the water flowing through the chambers,

- enzymatic reactions transforming drilling fluids into metabolites which are not detected in the chemical analyses and

- the net production within the chambers of reduced species, primarily sulphur, iron and manganese,

may contribute to the difference observed between the total loss given by the concentrations of drilling fluids and the respiratory loss calculated from sediment oxygen consumption measurements. The relative importance of these factors and how they may contribute to explain the variation of the respiration ratios given in Table 5, will be disussed in this section.

Barium analyses performed in test 3 gave an average loss of cuttings particles of 11% of the amounts added. Because this loss was independent on the type of drilling fluid it could not explain any variations between the respiration ratios for the various drilling fluids. Furthermore, all of the drilling fluids were highly insoluble in water and strongly attached to sediment particles. Thus, neither loss of cuttings particles nor dissolution and loss of drilling fluids proper via the water flowing through the chambers, were likely to explain any of the variation of the respiration ratios for the various drilling fluids.

Buried oxygen deficit in the Petrofree chambers may explain some of the unaccounted loss of this fluid. No attempt has been made to determine this deficit, but estimates based on characteristic rates of sulphate reduction and sediment iron reservoirs, indicate that iron reduction and ferrous sulphide precipitation might contribute significantly to an underestimation of the anaerobic respiration. Direct measurements of the flux of CO_2 performed once in all chambers towards the end of test 3, showed $O_2 : CO_2$ flux ratios reasonably close to the theoretical value of 1.0 (mean ratio = 0.97 with a standard deviation σ_{n-1} = 0.51 in n = 7 of total 8 chambers). However, a rather high ratio of 3.8 was observed in the Petrofree chamber which had had the highest oxygen consumption rates throughout the experimental period, and which towards the end of the experiment, obviously was experiencing a considerable chemical oxygen consumption driven by the oxygen deficit accumulated during an extensive degradation via sulphate reduction. However, the well balanced $O_2 : CO_2$ flux ratios, the only slightly lowered redox potentials as well as the absence of colour changes in any sediments other than those treated with Petrofree esters, showed that accumulated oxygen deficits were not likely to contribute significantly to the unaccounted loss of drilling fluids other than the Petrofree esters.

Thus, production of metabolites remains to represent the most significant process responsible for the lower range of respiration ratios given in Table 5. Mineral oil as determined by the non-specific THC-analyses is a complex mixture of species. Any metabolites of components of this mixture would have a better chance to show up in the chemical analyses than metabolites of the more homogenous synthetic drilling fluids analysed by highly specific GC-analyses. Thus, analytical procedures rather than differences with regard to initial enzymatic metabolite formation reactions, may explain the relatively high respiration ratios observed in the Mineral oil chambersTable 5.

Esters are known to be easily hydrolysed to yield an alcohol and a fatty acid. Fatty acids are easily available substrates for oxidation to CO_2 and water in the mitochondria of living cells. In the experiments, a time lag was found between the disappearance of the ester and the bulk of the oxygen consumption (compare Figure 2 and Figure 3). This was consistent with an initial hydrolytic cleavage reaction providing depletion of ester concentrations without a corresponding consumption of oxygen. The fact that high rates of oxygen consumption were observed for a long period of time after depletion of the esters, indicated that a large fraction of the degradable metabolites, rather than

becoming lost by dissolution to the overlying water remained present for degradation within the sediment.

Because of the lower precision level of the drilling fluid analyses in test 1, the respiration ratio of Novadril I was less certain than the respiration ratios of the other fluids. The low respiration ratio observed for the Aquamul ethers was, however, quite reproducible in the four chambers treated with this fluid. If, as compared to Novadril II, metabolite formation was a more important mechanism contributing to the enhanced loss rates of Aquamul ethers during the 60-180 days period, the lower respiration ratios as well as the lag phase required to obtain any reasonable fit of the Aquamul data to the exponential degradation model, would be expected. The formation of the metabolites may occur, e.g. by cleavage of the ether bond, independent of the oxygen consumption rates. The close similarity of the oxygen consumption rates in all treatments other than the Petrofree esters, indicated that the mineralisation rates for all drilling fluids other than Petrofree esters were controlled by a similar mechanism, most probably the stepwise oxidation of terminal carbon atoms in the hydrocarbon chains. Thus, as revealed by the GC-MS-analyses performed by SINTEF Industrial Chemistry, the absence of the double-bond first thought to be present at the terminal end of the Novasol II carbon chains, explained very well our failure to observe any enhanced mineralisation of Novadril II as compared to Aquamul ethers and Mineral oil.

Cleavage of ethers at the ether bond is expected to yield mostly alcohols. In general, alcohols produced by cleavage of ether bonds are thought to be less degradable than the fatty acids produced by cleavage of ester bonds. The absence of any increase of oxygen consumption rates in Aquamul chambers as compared to Mineral oil and Novadril II olefin chambers (Figure 3), did indeed show that unlike the ester metabolites, the ether metabolites were not easily degraded within the chambers. This might be a result of rapid loss of water soluble alcohols as well as slowly degradable compounds. In either case, the metabolites produced by the cleavage of Aquamul ethers are likely to remain present in the environment for a longer period of time than the metabolites of the Petrofree esters.

Conclusion of the benthic chamber studies

Conclusively, the benthic chamber experiments have shown that the Petrofree esters degrades much faster than any of the alternative drilling fluids. Little difference was found between Mineral oil, Aquamul ethers and Novadril II olefins, whereas the Novadril I olefins appeared to be the most slowly degrading fluid. However, as the Novadril olefins and the Aquamul ethers are more precisely known structures, the environmental behaviour of these substances can be more precisely predicted than the possible effects of the numerous components of mineral oil.

The major difference between the Novadril II and the Aquamul drilling fluids, appeared to be that of the lag phase and the lower respiration ratios of Aquamul, which may have resulted from more extensive degradation to ether metabolites.

As should be expected, the measured effects on redox potentials varied opposite to the biodegradation. All treatments provided negative E_h-deviations relative to non-treated control chambers. The maximum deviations (Table 5) as well as the frequency of significant negative deviations, were slightly larger for the Aquamul ethers as compared to Novadril II. This might be a result of the higher initial concentration. Initial pH anomalies (Figure 4) and some brittle star mortality has also been observed as effects occurring immediately after deposition of the Aquamul ether cuttings. However, these effects were all very moderate as compared to the lowering of the redox potentials observed in all chambers treated with Petrofree esters.

Field studies

Until now, available data on concentrations and biological effects of synthetic base muds from the North sea monitoring surveys are rather scarce.

Petrofree

At the Ula well site 7/12-9, 96.5 tons of Petrofree esters were discharged during a drilling operation in February-May 1990. As shown in Table 6 high concentrations of 85 300 mg·kg^{-1} esters were found in the sediments adjacent to the platform during the survey in 1990, and the macrobenthic community was strongly affected. Inspection and various analyses of the grab samples revealed a sharp boundary at about 100 m, beyond which no significant effects on the communities were observed (Smith and Moore, 1990). In 1991 and 1992 maximum concentrations of esters were 11.7 and 0.38 mg·kg^{-1}, respectively. Barium concentrations did not decrease correspondingly, showing that non-degradable mud components were left behind in the sediments. Thus the rapid disappearance of the esters could not have resulted from sediment migrations alone.

High densities of *Capitella capitata* were found at station SV/500 in 1991. In 1992 the diversity was high all over the sampled area (Table 6) and in fact, decreasing with increasing distance from the discharge point. Even though the Petrofree esters were almost completely depleted in less than one year after the discharge, multivariate analyses provided evidence that minor changes to the macrobenthic communities were still being caused two years after the discharge (Smith and Hobbs, 1993).

Table 6: Results from North sea monitoring at Ula well site 7/12-9.

Survey	Station	Esters mg·kg-^{1}	Barium mg·kg-^{1}	No. ind.	No. taxa	H(s)
1990	max. ester, SW 50m	85 300	1 720	16	4	1.50
1990	mean, 0-1km, n=8	16 546	1 546	231	39	3.63
1990	Ref., SW 5 km	2.3 (THC)	265	336	56	4.50
1991	max. ester, SE 100m	11.7	1 230	408	52	4.41
1991	mean, 0-1km, n=8	2.5	462	349	48	4.07
1991	Ref. NW 6 km,	0.25	78	329-340	48-58	4.18-4.73
1992	max. ester, SE 200	0.38	486	572	68	4.58
1992	mean, 0-1km, n=8	0.24	183	544	73	4.84
1992	Ref. NW 6000, A-B	0.09	55	465-475	68-72	4.46-4.48

At well site 2/7-22 south west of Eldfisk South, 135 tons of Petrofree esters were discharged during a drilling operation from May to October 1990. Only small amounts

of esters were recovered in the sediments during the monitoring survey in June 1991. Biological data were not available.

At Oseberg Field Center 70 tons of Petrofree esters were discharged after September 1991. During the survey in the following spring, benthic fauna were reported to be severely affected near the discharge point. Thus, severe effects occurred less than 8 months after the beginning of the discharge. In the benthic chamber experiments the time and magnitude of the sulphide event has been found to be dose-dependent and has been observed to last for up to 6 months after the discharge of one single batch of Petrofree cuttings (Figure 3). Thus, the timing and type of effects observed at Oseberg fits very well with the effects predicted from the timing and magnitude of the deviations of redoxpotentials observed in the benthic chambers.

Another discharge in June-September 1991, which contained 28 tons of mineral oil, has been suggested to contribute to the observed effects on the benthic fauna. Considering the moderate redox effects of mineral oil found in the benthic chambers, the smaller discharge and the longer time-lag after the discharge, it appears not very likely that the discharge of mineral oil was a primary cause of the observed effects on the benthic fauna at Oseberg in 1992. However, long-term effects of mineral oil has been observed. Thus, it cannot be ruled out that the discharge of mineral oil have contributed to the effects.

In 1993, most of the stations surrounding the Statfjord A platform were contaminated with Petrofree esters. The highest observed concentration was 47 000 mg·kg^{-1}. A clear reduction of the diversity of the benthic fauna was observed at the stations situated close to the platform (Kaarstad et al , 1994). However, as on the Oseberg field, effects of other discharges cannot be ruled out in this relatively old drilling location.

Daan et al, 1995, have recently reported a study of effects of the discharge of Petrofree esters on cuttings in the vicinity of well site K14-13 in the Dutch sector of the North Sea. Four months after the discharge, they found concentrations of esters up to 4700 mg·kg^{-1} dry sediments and a severe impoverishment of the macrofauna within 200 m from the discharge location. Eleven months after termination of drilling, maximum concentrations of esters had decreased to 250 mg·kg^{-1}. Significant effects on the macrobenthic communities could still be detected, but indications were found that recovery of the natural macrobenthic community had set in. The decline of concentrations of esters in the natural samples collected 1, 4 and 11 months after discharge yielded a mean half-life time of 133 days and a lower confidence limit of 68 days.

Thus, the data reported so far, seems to be fairly consistent with regard to severe biological effects in the vicinity of discharges of Petrofree ester cuttings. In the Dutch sector significant effects were still present 11 months after the discharge. At the Ula well site, indications were found for the presence of effects as long as two years after discharge. However, it appears that the esters disappear from the sediment at rates similar to those found in the benthic chamber studies and that the macrobenthic communities recover within a few years after the discharge.

Aquamul

Aquamul ethers were discharged at several fields in the North sea during the period 1990-1993. Only few results have been reported in the monitoring programmes. At the Gyda well site 2/1-9, 160 tons of ethers were discharged shortly before the survey in 1991.

During the following three years, at station 1 situated 50m SW from the platform, concentrations of Aquamul ethers were 2600, 14 700 and 3.7 mg·kg^{-1} in 1991, 1992 and 1993, respectively. The corresponding concentrations of barium decreased from 3850 mg·kg^{-1} in 1991 via 1960 mg·kg^{-1} in 1992 to 194 mg·kg^{-1} in 1993.

At stations 2, 3 and 9 situated 100-200m from the platform, mean concentration decreased from 236 mg·kg^{-1} in 1991 via 96 mg·kg^{-1} in 1992 to 2.1 mg·kg^{-1} in 1993. The corresponding decrease of barium was 1036 mg·kg^{-1} in 1991, 309 mg·kg^{-1} in 1992 and 205 mg·kg^{-1} in 1993. Both ether and barium concentrations exceeded back-ground levels in 1993. Thus, the decrease of the ether/barium ratio from $\geq 230 \cdot 10^{-3}$ in 1991 and 1992 to $\leq 19 \cdot 10^{-3}$ in 1993 showed that the entire reduction of Aquamul ethers was unlikely to have resulted from resuspension and current transport.

The absence of any significant decrease of ether concentrations observed between 1991 and 1992, and the very low concentrations found throughout the sampling area in 1993, indicated that a lag phase occurs before degradation of Aquamul ethers in the field as well as in the benthic chambers.

Bakke et al, 1992, noted that the biological effects of the high levels of ethers were remarkably weak. Only the 4 stations cited above (sts 1, 2, 3 and 9) were sampled at the Gyda well site in 1993 and biological effects were not reported.

Novadril

55 tons of Novasol II olefins were discharged from wells 1H and 3H at the Tordis field during drilling operations in 1993. Preliminary results from the monitoring survey in 1994, showed concentrations of Novasol II olefins of 1240-8920 mg·kg^{-1} at stations 5 and 1 situated 500 m downstream from the platform. At stations 2 and 6 situated 1000m downstream, concentrations were 32.5-81.8 mg·kg^{-1} and at a distance of 2000m in the same direction, the concentrations were <0.1 and 1.03 at stations 3 and 7, respectively. Results of the biological analyses were not available by the time of writing this report. These results may represent the first validation of possible biological effects of the Novadril II mud system on North Sea benthic communities.

Analyses of macrobenthic assemblages surrounding a Novadril well site in the Gulf of Mexico (Internal MI-document), showed that 24 months after the drilling operation concentrations ranged 560-19 110 mg·kg^{-1} (THC estimated from TPH-analyses) at a distance of 25 m. At 50m from the discharge site, concentrations were less than 3 620 mg·kg^{-1} and at 100-200 m concentrations ranged 20-720 mg·kg^{-1}. At a distance of 2000 m, concentrations were less than detection limit of 1mg·kg^{-1} at three of the four stations. At these three reference stations, 152-170 individuals of 27-32 species yielded diversities of 2.55-2.86. At the 14 stations with moderate levels of 20-1080 mg·kg^{-1}, 162-280 individuals of 26-38 species yielded diversities of 2.32-3.15.

Thus, Novadril olefins appears to remain present in the sediments for a long period of time. GC/MS scan of this Novadril mud showed that the primary components of the base fluid were C20 isomers similar to those of Novasol II. However, in addition to the C20 dimers, the US-version of the product contained a smaller fraction of the C30 trimer, which was not present in the Novadril II used in Europe. This difference might result in slower biodegradation of the US product.

The slight increase of the diversity indexes at stations having moderate levels of Novadril olefins, was comparable to the effects observed a long time after the depletion of Petrofree esters from the sediments at the Ula site in the North Sea. At both sites the effects might be considered an effect of the carbon energy added to the system by deposition of the drilling fluids. As shown, in the benthic chambers and apparently confirmed by the biological analyses at the Ula field site, this energy may remain active in the system for apparently long periods of time after the depletion of ester concentrations.

DISCUSSION

A major problem in the comparison of the environmental fate of the three Novadril mud systems was the fact that even though MI-Norge have brought forward results from a large number of environmentally relevant tests and investigations on toxicity, bioaccumulation and biodegradation, the results for one product could rarely be compared to the results obtained for another product because of either differences in test procedures or test organisms and/or the use of different test substances. Thus the octanol/water coefficient as well as the toxicity tests performed in 1990 by the LSR laboratories appears to have been performed on a fluid (AB-5243-SO) whose major components had much higher molecular weights than the major components of the three Novasol fluids.

Neither the results of the toxicity tests reported by CMS were fit for a comparison of the toxicity of the three Novasol products. Whereas both used mud and base fluid was tested for toxicity of the Novasol II products, unused mud were used as test substance for Novasol I and Novasol III. Furthermore, whereas the Novadril I was tested on *Skeletonema*, *Balanus* and *Mytilus*, Novadril III was tested on *Abra alba* and *Acartia* in addition to *Skeletonema*. Thus the only possible comparison was the test result of Novadril I and II on *Skeletonema*. This showed an EC50 of 5 275 mg l⁻¹ for Novadril II as compared to 2 100 mg l⁻¹ for Novadril I. The difference might, however, result from different composition of the mud systems as well as different toxicities of the base fluids. Much confusion might have been cleared away if the tests had been carried out using the same test organisms and comparable test substances, e.g. base fluids to test base fluid toxicity and cuttings to test toxicity of the actual outlet material.

Even though direct comparison of the three Novadril products could not be done from the results of the toxicity tests given by MI-Norge, the tests uniformly showed EC50 values much higher than the limits defined for moderate toxicity.

The BODIS tests on aerobic biodegradability also showed large variations, most of which could probably be ascribed to variations in test procedures. The tests on the three base fluid products performed by Rogalandsforskning, were reasonably consistent showing that Novasol III was slightly more degradable than Novasol II which again was more degradable than Novasol I.

Few known enzyme systems are capable to attack unsaturated hydrocarbons in the absence of oxygen (dissolved O_2-gas), and degradation of saturated hydrocarbons is thought to be strictly aerobic (Schink, 1988). Consistent with this knowledge, degradation tests performed by Rogalandsforskning, showed no degradation of Novadril II under anaerobic conditions. Thus, the 53-106% anaerobic degradation of Novadril I, as well as the 26-46% degradation of the saturated Novadril II base fluid, found by TNO, Holland, appeared rather controversial.

In their tests, degradation was calculated from the difference between gas production in replicate bottles treated with Novadril and control bottles without Novadril. Statistical analyses of the variance (ANOVA) of the gas volumes reported to be produced in

control bottles and bottles treated with Novadril I, showed that the small difference observed was not significant at the 95% significance level. Thus it appears important to conclude that no significant anaerobic degradation of the Novadril I test substance has been reported. No data were available to do a similar analyses on TNO`s test on Novadril II.

The recently reported 44-49% anaerobic degradation of Novadril III (Rogalandsforskning, 23.11.94) tend to confirm the expectations of improved degradability of the Novasol III base fluid, which is claimed to be composed of truly unsaturated and shorter chain poly-α-olefin compounds.

The benthic chamber studies showed that after deposition on a semi-natural sea-bed system, the Novadril I and II disappeared from the sediments with half-lives of 308 and 207 days respectively. In spite of the large scatter of the results of the chemical analyses of the Novadril I base fluids the different half-lives calculated by exponential regression analyses, did indicate an improved degradability of the Novadril II as compared to Novadril I.

As opposed to Mineral oil and Aquamul ethers, no lag phase could be assumed which would improve the correlation coefficient of the regression analyses. The total time required for the first halving of concentration was remarkably similar for these three fluids. Also respiration rates were almost identical throughout the experimental periods. Whereas the highly similar rates of oxygen consumption indicated similar hydrocarbon mineralisation rates, the lag phase as well as the lower respiration ratios found for the Aquamul chambers, may have been the result of more extensive metabolite production from the ether compounds.

Cuttings containing Petrofree esters gave much higher rates of sediment oxygen consumption than any other type of cuttings tested so far. Regression analyses on all data obtained until now, showed a half-life of 31 days. Regression analyses only on the most recent data gave residence times at about twice this value. Wether this difference was the result of improved test conditions or differences between different cuttings samples is not clear at the moment.

Esters are easily hydrolized to produce an alcohol and a fatty acid. Many fatty acids are easily transported across biological membranes and degraded to carbon dioxide and water in the mitochondria of living cells. If an initial cleavage reaction of the ester molecule, was followed by rapid aerobic and/or anaerobic mineralization of the cleavage products, the highest rates of oxygen consumption should occurr after the major decline of the concentration of esters. Such a time lag was indeed observed during several of the tests. This confirmed that the energy required for the intensive metabolic activity and proliferation of hydrogen sulphide in the pore waters in chambers treated with Petrofree esters was derived from metabolites produced by an initial cleavage of the ester molecule.

Even though careful examination of the results from the test on the Novadril II cuttings, revealed slightly larger and more frequent occurrence of negative redox potential deviations in chambers treated with Aquamul ether cuttings as compared to the chambers treated with Novadril olefins, these differences were small compared to the large negative deviations observed in chambers treated with Petrofree esters. Sulphide events were observed in all chambers treated with Petrofree esters. The negative effects of such events has to be evaluated against the effects of having the presence of slowly degrading fluid components for longer period of times.

Only a few data on synthetic drilling fluids have yet been obtained from the North sea surveys. So far, the results tended to confirm the rapid degradation of Petrofree esters as well as the severe biological effects predicted from the sulphide events observed in the

chambers. Also, the time lag before degradation of Aquamul ethers as well as the much weaker effects on macrobenthic communities reported from the North Sea, was consistent with the observations in the Aquamul chambers. With regard to Novadril olefins, no field data has yet been reported from the North Sea, but results from the Gulf of Mexico showed that two years after discharge, slightly increased diversities were observed in a relatively large area with moderate concentrations of Novasol PAO`s.

CONCLUSIONS

1. The Novasol fluids (I, II and III) are synthetic straight chain or slightly branched hydrocrabons, with or without a terminal double bond.
2. Test results reviewed above demonstrate a relative low toxicity of Novadril I and II muds to marine organisms as might be expected on the basis of their molecular structure and physical/chemical properties.
3. Recent results cited by MI, show similar low toxicity of Novadril III unused mud.
4. Calculated log P_{OW} values for Novasol II and longer chain PAO´s, indicate that little or no bioaccumulation should occur with the fluids proper. Neither seabed surveys nor experimental work have provided any evidence of bioaccumulation of Novasol I and II fluids in neither mussels nor fish.
5. Standard BODIS-tests performed at various laboratories have yielded 25-75% degradation of Novasol I, II and III during test periods of 28-157 days.
6. Tests performed by Rogaland Research showed that Novasol III degraded faster than Novasol II, and that Novasol II degraded faster than Novasol I.
7. In the absence of oxygen, degradation of Novadril I and II is still under discussion. Recent results on Novasol III showed a degradation of 44-49% during 69 days.
8. Tests performed under more natural conditions in benthic chambers, showed that Novasol II degraded with a halflife similar to those of Mineral oil and Aquamul ethers. Longer half-lives were found for Novasol I.
9. Effects on pH and redox potentials in sediments contaminated with cuttings containing Novadril I and II were less than the effects of any other drilling fluids tested.
10. Because of the low toxicity and the moderate effects on redox potentials, effects expected to occur on macrobenthic communities in areas contaminated with Novasol I and II should be less than those expected to occur from other drilling fluids tested.
11. So far, the few data reported on seabed effects of synthetic drilling fluids, tend to confirm the results obtained during the benthic chamber studies. This applies in particular to the rapid degradation and major redox effects of the Petrofree esters.

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[4] Because of an analytical error detected after completion of the report, a new version of the report will be prepared during the spring of 1995. Only corrected data and updated conclusions have been used in the present report.