

Main Office

P.O. Box 173, Kjelsås
N-0411 Oslo
Norway
Phone (47) 22 18 51 00
Telefax (47) 22 18 52 00
Internet: www.niva.no

Regional Office, Sørlandet

Televeien 3
N-4879 Grimstad
Norway
Phone (47) 37 29 50 55
Telefax (47) 37 04 45 13

Regional Office, Østlandet

Sandvikaveien 41
N-2312 Ottestad
Norway
Phone (47) 62 57 64 00
Telefax (47) 62 57 66 53

Regional Office, Vestlandet

Nordnesboder 5
N-5008 Bergen
Norway
Phone (47) 55 30 22 50
Telefax (47) 55 30 22 51

Akvaplan-NIVA A/S

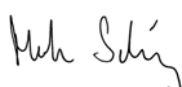
N-9005 Tromsø
Norway
Phone (47) 77 68 52 80
Telefax (47) 77 68 05 09

Title Bioavailability of metals in weight materials for drilling muds	Serial No. SNR 4597-02	Date 29.11.02
	Report No. Sub-No. O-21337	Pages Price 35
Author(s) Morten Schaanning Anders Ruus Torgeir Bakke Ketil Hylland Frode Olsgard	Topic group Micropollutants sea water	Distribution
	Geographical area North Sea Sediments	Printed NIVA

Client(s) Norbar Minerals AS	Client ref. Egil Mellgren
---------------------------------	------------------------------

<p>Abstract</p> <p>Bioaccumulation of metals from various weight materials used in drilling muds was determined after 28 days exposure of polychaetes (<i>Nereis diversicolor</i>) and gastropodes (<i>Hinia (Nassarius) reticulata</i>) to spiked sediments. The test was performed in a standard experimental set-up at Solbergstrand Marine Research Station and showed significantly higher concentrations of barium, titanium, lead, mercury and copper in organisms exposed to various test substances than in organisms exposed to non-spiked control sediments. Weaker evidence based on consistency between elevated bioaccumulation ratios and metal abundancies in the test substance, was found for iron, cadmium, chromium and nickel, but no evidence was found for bioaccumulation of zinc. Based on the experimental results on bioaccumulation of Hg, Cd, Cr, Cu, Ni, Pb and Zn, the five test substances were ranked in order from least to most harmful: Barite Zelmou < Hematite < Ilmenite < Barite Safi < Barite Zelmou/Safi. The report also provides a brief review of recent literature on biological effects of metals in drill cuttings, including relevant results from the UKOOA Drill Cuttings Initiative. The review suggest low to moderate toxicity to marine organisms and that most of the effects observed in field or mesocosm studies result from other mud components than metals in minerals used for weight material.</p>
--

<p>4 keywords, Norwegian</p> <ol style="list-style-type: none"> 1. Tungmetaller 2. Boreslam 3. Baritt 4. Marine sedimenter 	<p>4 keywords, English</p> <ol style="list-style-type: none"> 1. Heavy metals 2. Drilling mud 3. Barite 4. Marine sediments
--	---



Morten Schaanning



Kristoffer Næs



Jens Skei

Bioavailability of metals in weight materials for drilling muds

Preface

This report has been prepared on request from Norbar Minerals AS in accordance with our project proposal v.2, 23.04.02 and contract 21337.747/02 signed 25.04.02 and additional work proposed in e-mail 16.09.02. The experimental work was performed in the soft-bottom mesocosm laboratories at Solbergstrand Marine Research Station in June and October 2002 by Anders Ruus and Sigurd Øksnevad. Co-authors Torgeir Bakke, Ketil Hylland and Frode Olsgard have contributed on describing state of the art with regard to uptake and effects of heavy metals from drilling muds deposited on the seabed. Bente Hiort Lauritzen and co-workers prepared and performed all chemical analyses of sediments and biological tissues.

Oslo, 29.11.2002

Morten Thorne Schaanning

Contents

Summary	5
1. Introduction	7
2. Biological effects of metals from drill cuttings	8
2.1 Effects on marine benthic communities	8
2.2 Sublethal effects	9
2.3 The UKOOA Drill Cuttings Initiative	11
2.3.1 Metals in cuttings deposits	11
2.3.2 Metal bioavailability	11
2.3.3 Toxic effects	12
3. Experimental work	13
3.1 Objectives of the experimental work	13
3.2 Material and methods	13
3.2.1 Outline of method	13
3.2.2 Control sediment	13
3.2.3 Test substances	14
3.2.4 Organisms	14
3.2.5 Experimental set-up	14
3.2.6 Sampling	15
3.2.7 Chemical analysis	16
4. Results and discussion	16
4.1 Test substances and spiked sediments	16
4.2 Bioaccumulation	18
4.2.1 Al and Li - indications on depuration	19
4.2.2 Fe	22
4.2.3 Zn	22
4.2.4 Ba	23
4.2.5 Ti	23
4.2.6 Hg	23
4.2.7 Cr	23
4.2.8 Ni	23
4.2.9 Cu	24
4.3 Evaluation of test results	24
4.3.1 Evidence for bioaccumulation	24
4.3.2 Rank of test substances	25
5. Conclusion	27
6. References	28
Appendix A. Analyses in organisms	33

Summary

The drilling of wells in offshore oil and gas exploration produces significant quantities of waste. This waste (drill cuttings) is a mixture of crushed bore hole minerals and drilling muds added to optimize drilling performance. The major component of drilling muds is a solid phase (almost exclusively barite, BaSO₄) suspended in a fluid phase, which can be water or some organic phase (frequently an ester or C₁₂-C₁₈ olefins). Since 1990 discharge of muds based on mineral oil are no longer permitted in the North Sea. Sediments affected by discharged cuttings have frequently shown elevated concentrations of barium and potentially toxic metals such as lead (Pb), mercury (Hg) and cadmium (Cd), and adverse effects on benthic communities have frequently been documented.

The metals may originate in impurities in the barite minerals, in the bore hole materials or in other accidental discharges from the platform. Attempts to link concentrations of various heavy metals to the concentration of barium has proven difficult, probably because the metal content of barite as well as bore hole materials may vary according to the mineralogy of the specific barite source or formation drilled. Regardless of the source, it is not obvious that there is a causal relationship between elevated metal concentrations and the effects observed. The literature surveyed in the present report tend to suggest that toxicity or redox effects during biodegradation of the organic phase, physical change of the sediment substrate (e.g. grain size distribution) or simply particle loading, are more likely to explain adverse effects on benthic communities than heavy metal toxicity. Because metal concentrations in some off-shore deposits are above no-effect thresholds and because slow phase transformations may change metal bioavailability after discharge, metals cannot be completely acquitted from possible adverse effects on marine organisms. The present state of the art is, however, that evidence of such effects from metals associated with drill cuttings is scarcely found in the scientific literature.

A prerequisite of toxic effects is uptake in marine organisms. Therefore, an experiment was performed to compare bioaccumulation of metals from sediments spiked with barite from different ores (Barite Zelmou, Barite Safi and Barite Zelmou/Safi) and two alternative weight-materials for drilling muds, Ilmenite (an oxide of iron and titanium) and Hematite (an oxide of iron).

The test-substances were analysed for total metals after digestion with hydrofluoric acid and compared to Norwegian criteria for fjord and coastal sediments. According to this system, Hematite was “moderately polluted” with chromium (Cr) and Barite Zelmou was “moderately polluted” with copper (Cu). Ilmenite was “moderately polluted” with copper and nickel (Ni) and “markedly polluted” with chromium. Barite Safi was “moderately polluted” with copper and zinc (Zn) and “markedly polluted” with mercury (Hg), cadmium (Cd) and lead (Pb). Based on metal concentration, the Barite Zelmou/Safi test substance was ranked between the two other barite test substances.

The observed elemental composition of the Hematite and Ilmenite, showed that the test substances were representative with regard to previously reported composition of hematite and ilmenite. The composition of the three barite test substances varied within the same range as the metal concentrations in ship-loads of barite imported during the period 1994-2001. Thus the Barite Zelmou test substance was representative for ship-loads with a low content of metal impurities, whereas the Barite Safi was representative for ship-loads with higher content of metal impurities.

Two different species, the polychaete *Nereis diversicolor* and the gastropode *Hinia (Nassarius) reticulata* were exposed in seawater aquaria with a layer of sediment spiked with the test substance. After four weeks, metal concentrations in sediment and depurated biological samples were determined

after standard nitric acid digestion (NS4770). Analyses of aluminium (Al) and lithium (Li) indicated little bias from sediment contamination of the biological samples.

Ratios calculated between concentration in organisms exposed to spiked sediments and concentration in organisms exposed to non-spiked, control sediments, were used as indicators on bioaccumulation. Statistical analyses (ANOVA, Tukey HSD, $\alpha=0,05$ or Mann Whitney U-test) were applied to identify bioaccumulation ratios significantly larger than 1,0, i.e. the concentration in exposed animals were significantly higher than concentration in control groups.

Most of the 96 bioaccumulation ratios determined for the 10 metals (Fe, Ba, Ti, Hg, Cd, Cr, Cu, Ni, Pb and Zn) varied between 0,8 and 1,2. 29 ratios $\geq 1,24$ were considered to yield evidence for bioaccumulation.

Fifteen ratios ranging 1,26-259 showed significant bioaccumulation of titanium from Ilmenite, barium from all barite test substances, lead from Barite Zelmou/Safi and Barite Safi and mercury and copper from Barite Zelmou/Safi.

Six ratios ranging 1,26-1,78 were consistent with regard to metal enrichment in test substances and test sediments and bioaccumulation in both polychaetes and gastropods. These gave evidence for bioaccumulation of iron from Hematite, chromium from Ilmenite and cadmium from Barite Zelmou/Safi.

Seven ratios yielded weaker evidence based on a bioaccumulation ratio $\geq 1,24$ in one of the test organisms in combination with metal enrichment in the test substance. Such weaker evidence for bioaccumulation was found for iron, copper and nickel from Ilmenite, barium and chromium from Hematite and cadmium and mercury from Barite Safi.

One ratio of 1,24 had no supporting evidence and did not contribute to the ranking of the test substances.

No evidence was found for bioaccumulation of zinc from any of the test substances.

In ranking the least harmful weight substance, less weight was put on high bioaccumulation of low-toxic components such as Fe, Ti and Ba, than low bioaccumulation of the more toxic heavy metals (Hg, Cd, Pb, Cu, Cr and Ni). Organisms exposed to Hematite and Barite Zelmou yielded less evidence for bioaccumulation of the latter group of metals than organisms exposed to Ilmenite. On the other hand, organisms exposed to Barite Safi and Barite Zelmou/Safi yielded more evidence for bioaccumulation than those exposed to Ilmenite. Because of some evidence for bioaccumulation of chromium from Hematite, Barite Zelmou was considered slightly better than Hematite. If “<” means “slightly less than” and “<<” means “clearly less than”, the rank in order of the least harmful weight material was:

Barite Zelmou < Hematite << Ilmenite << Barite Safi < Barite Zelmou/Safi.

Even though major mineral components such as Ba, Fe or Ti or impurities such as Pb, Hg, Cd, Cu, Cr and Ni may be taken up in sediment dwelling animals, harmful effects on marine, benthic communities are difficult to distinguish from effects provoked by other mud components. Mesocosm experiments on soft bottom communities as well recent toxicity tests of off-shore sediment samples both conclude that organic phases are the most significant cause of adverse effects in areas contaminated with drilling muds. One study has related inhibited enzyme activity in turbot to uptake of lead after exposure to barite with high concentrations of lead, but evidence of adverse effects from metals in drill cuttings is scarcely found in the scientific literature.

1. Introduction

The drilling of wells in offshore oil and gas exploration generate significant quantities of wastes. This waste is made up of drilling fluids (muds) and the cuttings generated during drilling (Holdway 2002). There are three major types of drilling muds: water-based (WBM) where the fluid phase is water, oil-based (OBM) where the fluid phase may be diesel or low aromatic mineral oils, and synthetic-based (SBM) where mineral oil has been substituted with another organic phase such as an ester (Burke & Veil 1995). More recently, the term Organic Phase Drilling Fluid (OPF) has been introduced to apply to all chemicals based on an organic phase.

Common to all of these types is the presence of a weight material which is primarily present to provide sufficiently high density to stabilise the bore hole. Until now, barite (BaSO_4) has been almost exclusively used as weight material. The solubility of BaSO_4 is very low and because of the high concentrations of SO_4 in marine environments, concentrations of dissolved barium ions will be extremely low. The environmental concern has therefore been directed towards the toxicity of other heavy metals, primarily Hg and Pb, present as impurities in the barite. Recent initiatives have been taken within the oil industry to promote the use of alternative weight materials such as ilmenite (an oxide of iron and titanium) or hematite (an oxide of iron). In order to claim one material as less harmful to the environment than another, several issues needs to be adressed:

1. the concentration of the metals present in the weight material,
2. the general toxicity of the metals present,
3. their bioavailability and
4. their effects on marine organisms.

The objectives of the present investigation was to bring forward state of the art with respect to known effects on marine organisms of heavy metals from drilling muds and to perform a comparative study on the bioaccumulation of metals from sediments spiked with barite, ilmenite and hematite.

2. Biological effects of metals from drill cuttings

2.1 Effects on marine benthic communities

Discharges of contaminated drill cuttings have caused appreciable change of the benthos adjacent to many oil and gas platforms in the North Sea (Davies 1984, Gray et al. 1990, Kingston 1992, Olsgard & Gray 1995, Grant & Briggs 2002). In the worst affected areas, the fauna is of low diversity and dominated by opportunistic species. Further away from the platform, faunal diversity may be similar to that of the surrounding area, but with a detectable difference in species composition. At some sites, these changes in faunal composition are detectable as far out as 6000 m from the platform (Olsgard & Gray 1995).

Over the last years data on benthic communities around platforms where only water-based or synthetic drilling-muds have been used have become available. Preliminary results clearly indicate that the effects on the benthic fauna are less pronounced than those observed where oil-based drilling-muds were used (Jensen et al. 1999). Adverse effects on diversity of benthic communities could be shown at distances of 250 m from the platforms, in a few cases also at a distance of 500 m from the platforms. Increased abundance of a few tolerant species of benthic fauna could in a few cases be shown at distances of 1000 m. The results show that adverse effects were limited to an area of maximum 3 km² around each platform, compared to a maximum of 100 km² where oil-based drilling-muds were used.

Many platforms have large piles of cuttings lying beneath them. There is, however, a lack of consensus on which aspects of drill cuttings are responsible for the adverse ecological effects. One major area of potential impact of drill cuttings is from metals, which are associated with the drilling muds (Holdway 2002). Olsgard & Gray (1995) investigated effects on benthic communities from 14 oil and gas fields where oil-based drilling muds had been used. Correlation analyses between fauna and environmental variables indicated that the effects were mainly related to sediment content of total hydrocarbons, strontium and barium, but also to metals like zinc, copper, cadmium and lead. They concluded that the effects on the fauna were probably related mainly to oil, but also to barite and the heavy metal impurities it contains, which are discharged in the drill-cuttings. The metal content for zinc (Zn) and lead (Pb) in the sediments in several of the areas investigated in Olsgard & Gray (1995) were above the Apparent effects thresholds values given by Chapman (1992). The Apparent effects thresholds values are chemical concentrations that are observed or predicted to be associated with biological effects. This means that pollution effects related to metal content of these sediments cannot be excluded. However, possible effects of heavy metals on benthic communities are related to bioavailability of the metals, and the sediment metal concentration alone do not indicate that adverse effects are present. Whether the metals in these sediments were biologically available or not is not known.

Analyses of sediments showed that the barite spread slowly to greater distances over time also after cessation of drill-cuttings discharges. Subsequent to cessation biodegradation of oil and reduced concentrations of total hydrocarbons were observed in the outermost areas, but despite this there was an extension of areas where the fauna was effected. This may indicate that barite and related compounds, in addition to oil, also have an environmental impact (Olsgard & Gray 1995).

A number of experiments with organic phase drilling muds have been performed in benthic mesocosms at NIVAs experimental station at Solbergstrand outside Oslo, Norway. These studies have frequently shown that drilling-muds which are different with respect to organic phase (e.g. mineral oil, ether, ester or olefin), but similar with respect to weight material (always barite) produce different effects with regard to sediment oxygen consumption, redox potentials and benthic diversities

(Schaanning et al. 1996, Schaanning and Bakke, 1997). The effects observed in these experiments were consistent with field data reported by Daan et al. (1996) and Jensen et al. (1999).

One experiment performed with two different cuttings types contaminated with the same organic phase (olefins), but one with and the other without barite added, did not produce different deviations from control sediments (Schaanning, 1995). These experiments showed clear effects of the organic phase on the benthic ecosystem, but no evidence was found for any effects of barite.

Experimental work carried out by Tagatz and Tobia (1978), showed that the abundance of many species of annelids and molluscs were affected by high doses of barite on sandy sediments, more likely as a result of altered physical properties of the substrate than toxic effects of the barite. Similarly, Bakke et al. (1986) concluded from *in situ* recolonisation experiments that effects from water based muds on species composition, but not on species diversity, most likely resulted from physical factors such as altered grain size distribution. Hyland et al. (1994), concluded that significant reductions in abundances of hard-bottom species in the vicinity of an off-shore drilling operation, were primarily related to physical effects of increased particle loading.

A toxicity test of sediments from drill-cuttings around the North West Hutton platform in the North Sea concluded that hydrocarbons were the most significant cause of toxicity of the sediments contaminated with oil based drill cuttings (Grant and Briggs 2002).

2.2 Sublethal effects

In contrast to studies on community composition, there has been limited research on the sublethal effects of drilling mud components on marine benthic organisms. There are three main types of sublethal effects: (i) effects of particles, (ii) effects of oxygen-consuming material and (iii) toxicity from chemical components in the muds. The main focus here will be on the latter type of effects, i.e. toxicity. There are some studies that indicate stress from particles (e.g. Hamilton et al. 1981) and also sublethal effects of oxygen depletion (e.g. Hylland et al. 1996, Schaanning et al., 1996). Oxygen depletion is probably the main mechanism for community changes and is well covered by such studies and by the experimental studies referred to elsewhere in this report.

Barite is an essential component of most drilling muds. Primarily barium sulfate, barite also generally contains traces of other metals, e.g. lead (Pb) and copper (Cu). The degree of contamination by other metals depends on the source of the mineral. Barium itself is regarded as having low availability for uptake by organisms and has been used e.g. as a tracer for intestinal evacuation (Triadafilopoulos et al. 1998) and as X-ray contrast in implants (Isotalo et al. 1999). Barium is also known to interact with potassium channels and have been used in many studies to investigate this mechanism (see e.g. Colwell et al. 1992; Newman, 1989; van Driessche and Wolf, 1991). In addition, barium appears to interact with calcium-sensitive processes in cells (Hamano et al. 1991). Although barium is generally thought to have low toxicity, some studies do indicate that life-long exposure to barium may affect e.g. mammalian cardiovascular systems (Kopp et al. 1985).

There are two main questions concerning benthic effects of barite in drilling muds:

- (i) Are barium and the other metals bioavailable to benthic invertebrates and fish?
- (ii) Do barium and/or the other metals present in barite affect invertebrates and/or fish?

Results addressing the first question for sediment-dwelling invertebrates can be found elsewhere in this report. The limited number of other relevant studies can also be found there.

There exist a limited number of studies on the acute toxicity of drilling muds in general and barite specifically. Some studies indicate little effect (e.g. Carls and Rice, 1984; Clark and Patrick, 1987; Smith et al. 1982), whereas other studies indicate possible sublethal effects on growth in scallops (Cranford et al. 1999) and may cause morphological changes in gill cilia of bivalves (Barlow and Kingston, 2001). In freshwater, there are reported effects of barium on calcification in an algae (Prasad, 1984).

Some of the few available results on accumulation and effects of barite on fish derive from the feeding study with turbot (*Scophthalmus maximus*) by Farestveit et al. 1994. In that study, juvenile turbot was fed commercial fish feed spiked with either barite or ilmenite or barite + copper. The barite contained 5000 mgPb/kg which was an order of magnitude higher than the highest annual mean concentration in barites imported between 1994 and 2000 (see ch. 4.1, paragraph 1). The results from the chemical analyses were very variable and there were presumably some analysis and sampling artefacts. The results did however indicate that barium and lead accumulate in the liver and lead in blood following exposure for 10 weeks. Hepatic copper was also found in elevated concentrations in the group exposed to barite + copper. Turbot fed fish with ilmenite-spiked feed did not accumulate any of the metals analysed for (except possibly iron).

Sublethal effects of barite has to date been little investigated in fish. In the turbot study referred to above (Farestveit et al. 1994; Hylland, 1993), hepatic metallothionein was used as a marker for hypernormal metal accumulation in the liver. Metallothionein is a protein normally involved in zinc and copper metabolism and the levels will change if the intracellular metal¹ availability increases (Hodson, 1988; Hogstrand and Haux, 1991). There was however little evidence of increase of metallothionein in this feeding study. Copper is an essential element and levels are generally high in the liver of marine fish, so exposure must be high to cause accumulation and effects. A second contaminating metal from some sources of barite, lead, will not affect metallothionein, but may inhibit one of the enzymes of heme synthesis. The enzyme is δ -aminolevulinic acid dehydratase (ALA-D). There appeared to be some inhibition of the enzyme in the treatments with barite, indicating uptake and effects of lead in the turbot. There was also a clear negative relationship between blood lead concentration and ALA-D enzyme activity (Hylland, 1993).

Other studies have shown that inhibition of ALA-D in fish blood is a sensitive marker for environmental lead exposure (Hodson, 1976; Hodson et al. 1977; Johansson-Sjöbeck and Larsson, 1979; Krajnovic-Ozretic and Ozretic, 1980; Schmitt et al. 1984). In mammals and birds, this enzyme is limiting for the synthesis of heme (and thus hemoglobin). Chronic lead exposure will therefore cause anemia in birds and mammals. The enzyme does not appear to be rate limiting for heme synthesis in fish, however, so even long-term lead exposure (and strong inhibition of ALA-D) does not appear to affect hemoglobin levels (Haux et al. 1986).

The available studies indicate that exposure to high levels of barite, e.g. through feeding studies, may lead to bioaccumulation of associated metals (e.g. lead) that cause effects. In addition, some studies show effects of the barite or barium itself. In the studies concerning barite it is difficult to separate stress from particulate material from stress derived from soluble components. Studies with barium do indeed indicate that the divalent ion can affect biological systems, e.g. through interactions with ion channels or calcium signalling, but the relevance to environmentally exposed marine organisms is not clear.

¹ for metals such as copper, zinc, cadmium, mercury, gold, silver

2.3 The UKOOA Drill Cuttings Initiative

The United Kingdom Offshore Operators Association (UKOOA) has undertaken a research programme to tackle the historical issue of drill cuttings, which have accumulated beneath installations in the North Sea. The UKOOA Drill Cuttings Initiative was launched in June 1998 and completed in December 2001. The goal of the Initiative was to identify the best environmental practice and the best techniques available for dealing with these accumulations. The work was executed in two phases; Phase I essentially being a programme of desktop studies and Phase II including recovery of cuttings material for laboratory experiments plus some limited offshore field trials to provide data for comparative assessment of different management options. Through the large number of studies executed under the Initiative some information on metal contents of cuttings discharges and their potential bioavailability and environmental effects have been produced. The focus of the initiative has been on historical drill cuttings deposits on the sea floor, where the metals may originate from other sources in addition to impurities in barite and other drilling mud weighting agents, primarily the rock cuttings themselves (Li and Fe) and produced water (Hg, Zn and As). The results are still considered relevant for the present assessment since the bulk of the metals in the cuttings deposits are believed to come from the drill mud (UKOOA 2001).

2.3.1 Metals in cuttings deposits

There are several sources to the metal content of drill cuttings deposits in the North Sea in addition to the drilling mud weighting material. One of the studies (Westerlund et al. 2001) focused on chemical composition of existing cuttings deposit piles. Two medium sized piles were investigated, one representing a typical situation from drilling with oil based fluids, the other from drilling with synthetic fluids. The piles differed in horizontal and vertical distribution of heavy metals, which could be expected due to different drilling histories, but the overall metal contamination pattern was similar. Generally most metals of environmental concern were found at elevated concentrations compared to background levels. Most concentrations were within class I or II (insignificantly to moderately contaminated) according to Norwegian quality criteria for fjord and coastal sediments (Molvær et al, 1997), except for Pb that had concentrations corresponding to class III (markedly polluted). There was no apparent correlation between Pb and Ba, suggesting different kinetics of the two elements, and presumably variation in Pb impurity of the sources of barite used over time. Hence, although drill cuttings deposits of various origin contain elevated levels of several metals, the levels seem not to be substantially high, and seem not to be easily linked to the content of barite alone (as expressed by the content of Ba).

2.3.2 Metal bioavailability

From the literature surveys forming the main activity of Phase 1 of the UKOOA Initiative it was concluded that “Experimental evidence demonstrated low bioavailability of heavy metal elements within a cuttings pile and very low levels of heavy metal leaching from a cuttings pile” (UKOOA 2001). This was followed up by several studies during Phase II of the Initiative. In one study (Westerlund et al. 2001), sequential extraction of metals from the cuttings material was used to obtain information on potential mobility during various geochemical processes, which again might suggest differences in bioavailability of cuttings pile metals if exposed to the water. For the metals of high environmental concern (Hg, Pb and Cd) the largest fraction was bound in a state suggesting high geochemical mobility, hence possibly high bioavailability. The results also showed that for the cuttings material with the highest total concentrations of these metals, less of the metals were in the “labile” state.

In other studies under the UKOOA Initiative the mussel *Mytilus edulis* was found to accumulate Pb, Zn, Cd and Hg from oil based cuttings in mesocosms (URS and TNO 2001). However, a generally similar pattern was observed for a North Sea reference sample. The same trend was found for the polychaete *Nereis virens*, whereas a slight accumulation of Pb from water based cuttings was found in

the turbot *Scophthalmus maximus* (URS and TNO 2001). This suggests that no substantial bioaccumulation of metals occurred from exposure to oil based cuttings versus reference sediment, but the results were somewhat inconclusive since the reference sediment also contained relatively high levels of metals as well. Lack of bioaccumulation of metals from oil based drill cuttings was also found in 3 sediment living species (the lugworm *Arenicola marina* and the bivalves *Macoma balthica* and *Cerastoderma edule*) in an earlier joint industry project (E&P Forum 1996).

2.3.3 Toxic effects

One way to separate toxic effects of drilling fluid metals from that of other drill mud components, primarily hydrocarbons or synthetics in base fluids, might be to study the toxicity of water based muds and cuttings. Under the UKOOA Initiative one study (ERT 2001) focused on the toxicity of water based cuttings sampled from existing North Sea piles, using the amphipod *Corophium volutator* and the microalga *Skeletonema costatum* as test organisms. The toxic responses in *C. volutator* were consistent with what would be expected for material containing corresponding levels of hydrocarbons as those found in the WBM samples tested (approximately 100 mg/kg dry weight). The results therefore provided no evidence to indicate significant added influence of other components in the cuttings (such as metals). The algal test applied a water elutriate of the test material, and the results obtained indicated absence of significant quantities of soluble toxicants in the water based cuttings supplied. Also in another study under the Initiative (URS and TNO 2001) no toxic response to water based cuttings was found neither to *C. volutator* and the sea urchin *Echinocardium* sp. (whole cuttings) nor to the zooplankton copepod *Acartia tonsa* (elutriate of the cuttings). Lack of apparent adverse effects of metals in cuttings to marine organisms also conforms to most earlier findings (e.g. Bakke et al. 1986; E&P Forum 1996).

3. Experimental work

3.1 Objectives of the experimental work

Knowledge of the bioavailability of potential environmental contaminants is relevant both with regard to ecology and to human consumption of marine organisms. Such knowledge can not be obtained merely by chemical analysis of contaminants in sediments and biota. Causes for this are, among other factors, that different physico-chemical properties of different contaminants (e.g. lipophilicity and recalcitrance against biological degradation) in addition to properties of the sediment, such as particle size and organic content, will affect the bioavailability. These factors also make it difficult to extrapolate results from studies of specific compounds to other contaminants. It is therefore most adequate to evaluate bioavailability by direct measures of bioaccumulation of specific compounds in bottom dwelling organisms. Such bioavailability studies have been conducted in several countries, in most cases as a tool in the assessment of the environmental risk of dredged sediment. The most comprehensive documentation from such tests has been produced by the U.S. Environmental Protection Agency (Lee et al. 1991).

The objective of this experiment was to evaluate the bioavailability of selected elements² in sediments spiked with hematite, ilmenite or one of three different types of barite (Figure 1).

3.2 Material and methods

3.2.1 Outline of method

The experiment was performed in the soft-bottom mesocosm laboratories at Marine Research Station Solbergstrand using a standardised set-up for testing the bioavailability of environmental contaminants in marine sediments (Hylland, 1996). The test is performed in 15 × 20 × 22 cm glass aquaria with a bottom layer of ca 1,5l sediment covered by a continuously flushed layer of seawater supplied from 60 m depth in the Oslofjord nearby the mesocosm facility. Sediment-dwelling test organisms are exposed for a period of 28 days (Lee et al., 1991) in replicate aquaria with non-spiked control sediments and sediments spiked with the test substance. After the exposure period, test organisms are removed from the sediment and depurated in sea water before analyses of contaminants.

The method is described in detail by Hylland, 1996. The test system has earlier been applied in tests on bioavailability of organic contaminants and/or metals in sediments from Florvågen (Bergen) (Knutzen et al. 1995), Drammensfjorden (Skei and Andersen, 1996) and Kristiansandsfjorden (Oug et al. 2002), in addition to tests on bioavailability of copper (Cu) from a net cleaning facility (Johnsen et al. 1996).

3.2.2 Control sediment

Sediment for the experimental work was collected in Rambergbukta, a bay located on Jeløya in the outer Oslofjord. The location is previously documented to have low background concentrations of metals and organic pollutants (Johnsen et al. 1996, Oug et al. 2002). One batch of sediment collected in May (Control I) had an organic carbon content of 5,3 µg/mg dry sediment and 73 % of the particles were smaller than 63 µm. Metal concentrations are given in Table 1. The second batch collected at the

²Mercury (Hg), Lead (Pb), Cadmium (Cd), Chrome (Cr), Copper (Cu), Nickel (Ni), Zinc (Zn), Barium (Ba), Titanium (Ti), Iron (Fe), Aluminium (Al) and Lithium (Li).

same location in October (Control II) had a higher concentration of Hg, but with regard to all other elements determined, the two batches of control sediments were very similar. The sediment was homogenised using a cement mixer (used only for sediments) before initiation of the experiment.

3.2.3 Test substances

The five test substances Barite Zelmou, Barite Safi, Barite Zelmou/Safi, Hematite, and Ilmenite, were supplied from Norbar Minerals AS. The test substances appeared as dry, powdered stone material, presumably identical to the products used in various mud formulations.

Before initiation of the experiment, aliquots of the homogenised control sediment were spiked with the various test substances in a 4:1 volume:weight ratio (litres of wet control sediment:kg of dry test substance). The mixtures were homogenised using a mechanical stirrer (paint mixer used for sediment mixing only). Approximately 0.5 L seawater was added to each of the mixtures to facilitate homogenisation.

3.2.4 Organisms

The test organisms were collected on the same location and at the same times as the collection of control sediments. Before use, the organisms were acclimated in the laboratory for about one week.

Two species were used in the experimental set-up, the ragworm, *Nereis diversicolor* (Polychaeta) and the netted dog whelk, *Hinia (Nassarius) reticulata* (Gastropoda). The polychaete (*Nereis diversicolor*) is common along the coasts of Europe, from the Mediterranean to Helgeland (Norway), and in the Baltic Sea. It is found primarily in shallow waters, where it can exist in dense populations. The netted dog whelk is also found in shallow waters. This species is common from the Canary Islands and the Azores in the south, to Lofoten (Norway) in the north. Both the ragworm and the netted dog whelk prefer sandy or muddy sediment and are tolerant to low salinities. Neither the polychaete nor the gastropod live directly of the sediment. The polychaete is omnivorous (Goerke, 1971), but most likely feeds on smaller organisms. The netted dog whelk is a scavenger and a predator, but can also utilise organic matter in the sediment. The ragworm is one of the most studied marine invertebrate and has also been used in other bioaccumulation studies (Fowler et al. 1978; Goerke, 1984). Sediment dwelling organisms, such as *Nereis* and *Hinia* are important prey items to several bottom dwelling fish species, and may therefore contribute to the transport of contaminants to higher levels in the food chain (Ruus, 2001).

The reason for using two organisms is that species specific differences may exist, regarding bioaccumulation of environmental contaminants. Polychaetes and molluscs represent two important groups in marine ecosystems.

3.2.5 Experimental set-up

Two successive tests were performed following identical procedures and using the same equipment, mesocosm location and sea-water source. Control sediments and organisms were sampled at the same field location a few days before the establishment of the respective test.

The first test was performed during the period 27.05.02-24.06.02 and used a set-up of twelve glass aquaria, i.e. three replicates of each of four treatments: non-spiked control sediment and control sediment spiked with either Hematite, Barite Zelmou or Ilmenite. The second test performed during 27.09.02-25.10.02 encountered nine aquaria with the same number of replicates of control sediments, and control sediments spiked with Barite Zelmou/Safi or Barite Safi.

3.2.6 Sampling

After exposure for 28 days, the organisms were collected from the tanks. The polychaetes were held in a beaker of seawater for 6 to 8 hours to empty all remnants of sediments from the intestines (Figure 3). The soft parts of the gastropods were separated from their hard shell. The soft tissues were then transferred to glass containers and stored at $-20\text{ }^{\circ}\text{C}$ before chemical analysis. All individuals of the same species from each aquarium were pooled into one sample.



Figure 1. From left: Control (unspiked) sediment and sediment spiked with ilmenite, hematite and barite.

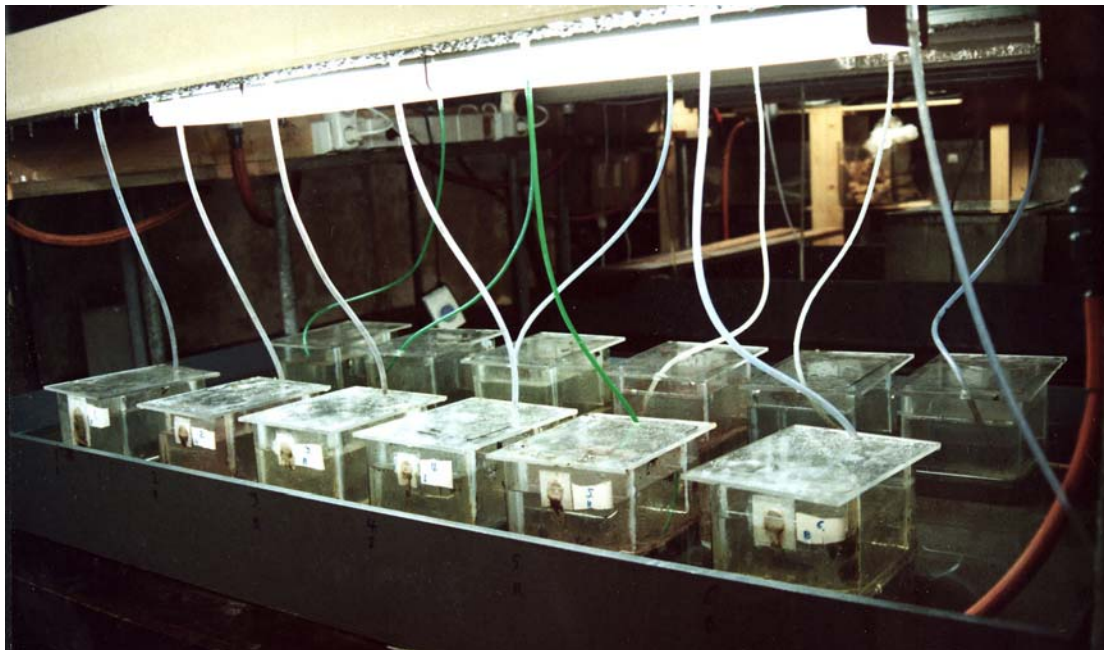


Figure 2. The experimental set-up involved a total of 21 glass aquaria (three replicates x five test substances and two controls).



Figure 3. Ragworms, *Nereis diversicolor* (Polychaeta) held in beakers of seawater to empty the intestine from sediment residues.

3.2.7 Chemical analysis

The chemical analyses were performed at NIVA's laboratory. The test substances were analysed after dissolution in aqua regia with hydrofluoric acid in microwave oven (Loring and Rantala, 1989). The procedure is generally accepted to yield total concentration of metals, but even this treatment may be inadequate for complete dissolution of some components (e.g. BaSO_4).

Spiked sediments and biological samples were analysed after dissolution in HNO_3 at 120°C (NS4770). With this method, strongly bound metals e.g. in lattice structures, may remain particle bound and escape detection.

Analyses of mercury (Hg) and cadmium (Cd) in sediment extracts were performed using cold vapour technique and graphite oven, respectively. All other metals extracted from the test substances and sediments were detected using ICP. The biological samples were determined using ICP-MS for all metals except Hg which was determined using the cold vapour technique.

4. Results and discussion

4.1 Test substances and spiked sediments

Element concentrations in test substances and spiked sediments are shown in Table 1.

The representativity of the test substance is important for assessment of test results. Therefore, data on shiploads of barite imported during the period 1994-2001 was supplied from the contractor. These data showed considerable variability, which probably results from different origin of the sample (Leuterman et al. 1997). As shown in Table 1, metal concentrations in the Barite Zelmou/Safi was fairly similar to the weighted annual mean concentration in ship-loads of barite imported to Norway during 2001 (Norbar Minerals, analytical reports 01.02.02). Concentrations in Barite Safi were frequently higher and concentrations in Barite Zelmou was frequently lower, than the weighted average of barite imported during 2001.

Table 1. Literature data and observed concentrations (mg/kg) in test substances and spiked sediments (note different digestion techniques based on either nitric or hydrofluoric acid) compared with national criteria (insignificantly, moderately or markedly polluted) for coastal and fjord sediments (Molvær et al., 1997). Criteria are not defined for Al, Li, Fe, Ti and Ba. Observed concentrations are also shown as % of the concentration expected from the mixing ratio between control sediment and test substance. Grey shading suggest samples with low yield of the HNO₃ extraction.

	Al	Li	Fe	Ti	Ba	Zn	Hg	Cd	Pb	Cu	Cr	Ni	As
<i>Norwegian classification criteria for coastal and fjord sediments</i>													
Class I "Insignificantly polluted"						<150	<0,15	<0,25	<30	<35	<70	<30	20
Class II "Moderately polluted"						150-700	0,15-0,6	0,25-1	30-120	35-150	70-300	130-600	
Class III "Markedly polluted"							0,6-3	1-5	120-600		300-1500		
<i>Test substances (literature data) (digested with HNO₃)</i>													
Barite, mean conc. in shiploads imported 2001 ³						42,9	0,307	0,7	54,5	76,6	13,1	1,2	
Ilmenite ⁴	830	-	3400	-	-	5,0				3,2	1,9	1,4	
Hematite ⁵	1800	-	51000								5,3		
<i>Test substances (digested with HF)</i>													
Barite Zelmou	1370	2	24800	28,6	9700	35	0,13	0,06	10	74	19	3	2
Barite Zel./Safi	2330	2	26500	na	9220	197	0,37	0,77	130	100	18	4	na
Barite Safi	3480	4	8680	na	8950	182	1,81	1,08	230	91,8	14	3	na
Ilmenite	3570	2	345000	252000	1500	100	0,005	0,03	8	37,5	469	147	<2
Hematite	5660	2	221000	904	5970	10	0,009	0,03	10	11	156	10	<2
<i>Control and spiked sediments (digested with HNO₃)</i>													
Barite Zelmou	7200	11	12800	616	7320	34	0,083	0,06	8,4	17,2	16,6	12	
Barite Zel./Safi	6540	10	12300	na	7780	62,6	0,1	0,15	39,5	23,7	16,4	11,6	
Barite Safi	7080	10,5	11700	na	7030	57,9	0,4	0,19	46,2	21,2	17,2	12,2	
Ilmenite	7590	11	14600	980	269	33	0,02	0,049	6,2	10,8	21,4	18,3	
Hematite	7520	11	18000	632	890	33	0,018	0,046	6,7	8,95	33,3	13,9	
Control I	8620	13	14100	707	56,6	36,7	0,019	0,05	7	8,92	17,4	14,5	
Control II	7920	12	13400	na	56,5	38,3	0,1	0,04	9,8	9,14	17,1	13,7	
<i>Observed/predicted</i>													
Barite Zelmou	100 %	102 %	79 %	108 %	369 %	94 %	201 %	115 %	111 %	78 %	94 %	98 %	
Barite Zel./Safi	96 %	100 %	77 %	-	412 %	89 %	65 %	81 %	117 %	87 %	95 %	99 %	
Barite Safi	101 %	101 %	94 %	-	383 %	86 %	90 %	77 %	86 %	83 %	104 %	106 %	
Ilmenite	100 %	102 %	18 %	2 %	78 %	67 %	123 %	107 %	86 %	74 %	20 %	45 %	
Hematite	94 %	102 %	32 %	85 %	72 %	105 %	106 %	100 %	88 %	96 %	74 %	102 %	

³ Norbar Minerals, analytical report 01.02.02.

⁴ West Lab Services, analytical report, 03.08.01.

⁵ West Lab Services, sample no. 2001-02726-1.

The composition of the ilmenite test substance was very similar to that of a “...typical sample of Tellnes ilmenite concentrate” cited in several papers (Fjogstad et al. 2000, 2002 and Saasen et al. 2001). Previous analyses performed using HNO₃ digestion (Table 1) showed much lower concentrations of Al, Fe, Zn, Cu, Cr and Ni, but similar concentrations of Hg, Cd and Pb. This difference might of course result from occasional variations between samples from different ores, but is more likely to result from different digestion methods. Fractions insoluble in nitric acid may contribute to higher concentrations in the same material analysed after digestion in hydrofluoric acid.

Similarly, a previously reported sample of hematite analysed with HNO₃ digestion (NS4770), showed lower concentrations of Al, Fe, and Cr than those obtained with the total extraction procedure (Table 1), but similar concentrations of Zn, Hg, Cd, Pb, Cu and Ni. It appears that the major fractions of Al, Fe, Zn, Cu, Cr and Ni in Ilmenite and Al, Fe and Cr in Hematite are strongly bound to mineral particles and not available for HNO₃ digestion in accordance with NS4770.

The analyses shown in Table 1 yield a second indication on the presence of fractions insoluble in nitric acid. From the 4:1 mixing ratio between control sediment and test substance, the predicted concentration in the spiked sediment was calculated from the concentrations observed in the test substances (using HF) and non-spiked control sediments (using HNO₃). The last 5 rows in Table 1 show the observed concentration in % of the predicted concentration. Deviations from 100% reveal any errors in dilution, mixing, sampling and analyses, but low yields most likely result from incomplete dissolution of mineral fractions in the HNO₃ extraction. Thus, low yields indicated the presence of significant insoluble (in HNO₃) fractions of Fe in hematite and Fe, Ti, Cr and Ni in ilmenite.⁶

The results from the HNO₃ extractions performed on different samples at West Lab and NIVA were consistent with regard to the presence of strongly bound fractions of Fe, Zn, Cu, Cr and Ni in ilmenite and Fe and Cr in hematite. Titanium was not analysed by West-lab, but low yields (Table 1) of this element in HNO₃ applied to all test substances and ilmenite in particular.

Compared to national environmental criteria for coastal and fjord sediments (Molvær et al. 1997), the data given in Table 1 shows that hematite was moderately polluted with chromium. Ilmenite was moderately polluted with copper and nickel and markedly polluted with chromium. The Barite Zelmou was moderately polluted with Cu, whereas the Barite Safi was moderately polluted with Cu and Zn and markedly polluted with Hg, Cd and Pb. In the sediments spiked with Barite Safi only Pb and Hg exceeded the upper limit of class I.

4.2 Bioaccumulation

Metal concentrations and standard deviations for the organisms living in the different sediments are shown in Appendix A. Figure 6 and Figure 7. BioAccumulation Ratios (BAR) (Table 3, Figure 4 and Figure 5) were calculated as the ratio between concentration (C) of the actual metals (Me) in organisms from spiked sediments (SS) and the corresponding concentration in animals from control sediments. For example, the bioaccumulation ratio for metal Me in polychaetes exposed to Ilmenite is:

$$\text{BAR}_{\text{Me,ilmenite, polychaete}} = C_{\text{Me,polychaete, ilmenite}} / C_{\text{Me,polychaete, control}}$$

⁶ Positive deviations for barium in all barite types and mercury in Barite Zelmou have no obvious explanation, but may result from sample inhomogeneities or analytical errors. Barium is known to be incompletely detected even in the aqua regia with HF extraction and the presence of sulphate in sea water media is a very strong ligand for barium precipitation.

Both concentrations were mean values of the three replicate aquaria. Ratios >1,0 indicate bioaccumulation. For comparison, Table 3 also show Sediment Enrichment Ratios (SER) calculated as the ratio between metal concentrations ($C_{Me, sed.}$) in spiked sediments and metal concentrations in control sediments. For example, the sediment enrichment ratio for metal Me in sediments spiked with Ilmenite is:

$$SER_{Me} = C_{Me, sed, ilmenite} / C_{Me, sed, control}$$

Statistical analyses (ANOVA, Tukey HSD, $\alpha=0.05$) were performed to identify significant differences between metals in organisms exposed to spiked sediments and organisms exposed to control sediments. Where heterogeneity in variance between groups was high, the Mann Whitney U-test was applied. Since the study was performed as two successive tests, the statistical analyses were done separately for Hematite, Ilmenite, Barite Zelmou vs Control I and Barite Safi, Barite Zelmou/Safi vs Control II. Biaccumulation ratios significantly >1,0 ($p < 0,05$) are highlighted in Table 3.

4.2.1 Al and Li - indications on depuration

Complete depuration of metals from body surface and intestine of experimental animals is often difficult to obtain, but nevertheless important to avoid erroneous results in bioaccumulation tests. If a small clot of sediment is present in the biological sample, the concentration of elements with high concentration in the sediment may provide overestimated BAR-values and false evidence on bioaccumulation.

Metals with particularly high concentrations in sediments as compared to biological tissues are best suited for identifying sediment contamination. Similar concentration in all test sediments is another criterium making an element suitable for identification of sediment contamination. Of the metals analysed in this study, Al and Li met fairly well with both criteria. Both elements were fairly even distributed in test substances and test sediments (Table 1), and as shown in Table 2, Al had the highest sediment:organism ratio for both polychaetes (253) and gastropods (65). Also Li had relatively high sediment:organism ratios.

Table 2. Ratios between concentrations measured in sediment (mean of all samples) (dry wght.) and concentrations in organisms (mean of all samples) (wet wght.).

	Sediment:Polychaete concentration ratio	Sediment:Gastropode concentration ratio
Al	253	65
Ti	152	27
Pb	145	53
Fe	125	42
Li	74	50
Cr	52	40
Ni	42	11
Ba	27	18
Hg	12	4
Cu	7	0,5
Cd	6	0,1
Zn	2	0,4

Table 3. Metal enrichment ratios (SER and BAR, see text) after exposure in sediments spiked with hematite, ilmenite and three types of barite. Shading shows BARs significantly >1,00 (p<0,05). Numbers in parenthesis shows the ratio calculated without correction for one polychaete sample contaminated with sediment.

Element	Sample		B.Zelmou	B. Zelmou/Safi	B. Safi	Hematite	Ilmenite
Al	sediment	SER	0,84	0,83	0,89	0,87	0,88
“	polychaete	BAR	1,33	0,83	1,99 (2,58)	0,62	1,54
“	gastropod	BAR	0,75	1,23	1,11	0,67	0,93
Li	sediment	SER	0,85	0,83	0,88	0,85	0,85
“	polychaete	BAR	0,89	0,92	1,04 (1,28)	0,78	0,89
“	gastropod	BAR	0,84	1,11	1,06	0,70	0,87
Fe	sediment	SER	0,91	0,92	0,87	1,28	1,04
“	polychaete	BAR	1,14	1,03	1,40 (1,76)	1,39	1,46
“	gastropod	BAR	0,83	1,17	1,09	1,30	1,05
Ti	sediment	SER	0,87	na	na	0,89	1,39
“	polychaete	BAR	1,19	na	na	0,78	5,66
“	gastropod	BAR	1,15	na	na	0,94	2,16
Ba	sediment	SER	129	137	124	15,7	4,75
“	polychaete	BAR	66	102	259 (342)	0,76	0,95
“	gastropod	BAR	75	33	25	1,47	0,78
Zn	sediment	SER	0,93	1,63	1,51	0,90	0,90
“	polychaete	BAR	0,93	1,04	1,00 (1,18)	1,06	1,12
“	gastropod	BAR	0,75	1,07	0,90	0,97	0,88
Hg	sediment	SER	4,37	1,68#	6,72#	0,95	1,05
“	polychaete	BAR	0,90	1,26	1,25 (1,53)	0,83	0,87
“	gastropod	BAR	0,89	1,41	1,04	1,23	0,89
Cd	sediment	SER	1,20	3,75	4,75	0,92	0,98
“	polychaete	BAR	0,93	1,61	1,27 (1,61)	0,93	0,98
“	gastropod	BAR	0,68	1,78	1,09	0,86	0,59
Pb	sediment	SER	1,20	4,03	4,71	0,96	0,89
“	polychaete	BAR	1,11	2,46	5,06 (6,73)	0,81	1,16
“	gastropod	BAR	0,86	2,52	2,79	0,73	0,82
Cu	sediment	SER	1,93	2,59	2,32	1,00	1,21
“	polychaete	BAR	1,15	1,04	1,16 (1,39)	0,88	0,98
“	gastropod	BAR	0,73	1,49	0,67	1,23	1,24
Cr	sediment	SER	0,95	0,96	1,01	1,91	1,23
“	polychaete	BAR	1,04	1,08	1,13 (1,42)	0,99	1,26
“	gastropod	BAR	0,88	0,77	0,65	1,36	1,40
Ni	sediment	SER	0,83	0,85	0,89	0,96	1,26
“	polychaete	BAR	1,05	0,93	1,03 (1,25)	0,95	1,29
“	gastropod	BAR	0,83	1,00	0,96	0,66	0,69

#calculated against mean sediment concentration for control I and II

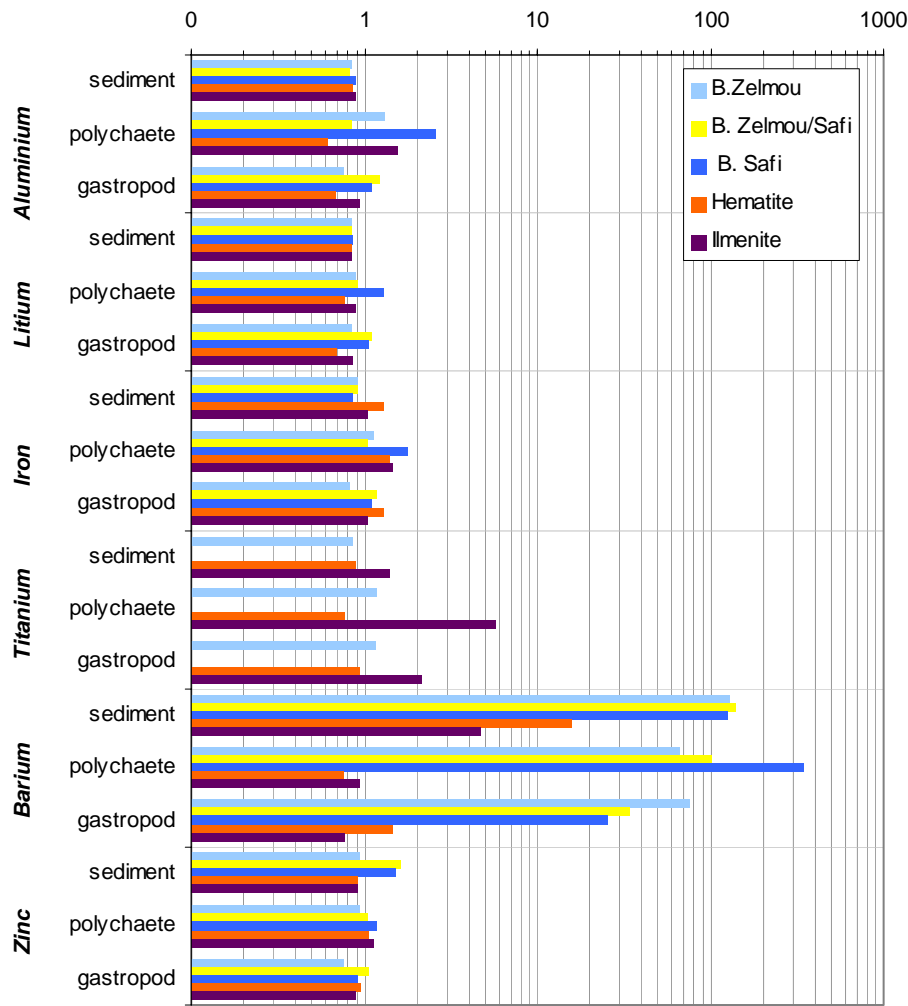


Figure 4. Metal enrichment ratios (SER and BAR for Al, Li, Ba, Fe, Ti and Zn) in organisms after 28 days exposure in control sediments or sediments spiked with test substances. Note logarithmic scale.

All test substances gave sediment enrichment ratios for Al and Li between 0,83 and 0,89 (Table 3, Figure 4) whereas the bioaccumulation ratios varied between 0,62 and 2,58 for Al and 0,70 and 1,28 for Li. The highest ratios for both elements were found in the polychaetes from the Barite Safi treatments. As shown in Appendix A. Table 6 the concentration of Al in the second replicate was 102 $\mu\text{gAl/g}$ as compared to 47 and 49 $\mu\text{gAl/g}$ in the other two samples and a grand mean of $30 \pm 24 \mu\text{gAl/g}$ (\pm one standard deviation) for all polychaete samples. The lack of supporting evidence from analyses of gastropodes, sediments or test substance suggested that the high concentration of Al and Li in polychaetes from the Barite Safi aquaria was a result of incomplete depuration in one of the samples rather than bioaccumulation of Al. The contaminated sample contained in average 79,8% more Al and Li than the two other replicates. The metal concentrations in this sample was therefore corrected by dividing with 1,798 for calculation of bioaccumulation ratios and statistical analyses. Uncorrected data are shown in Appendix A. Table 6 and in the parentheses in the column for Barite Safi in Table 3.

The fact that this sample was the only one producing severely elevated BARs of both Al and Li indicated that depuration had been complete in most of the other samples.

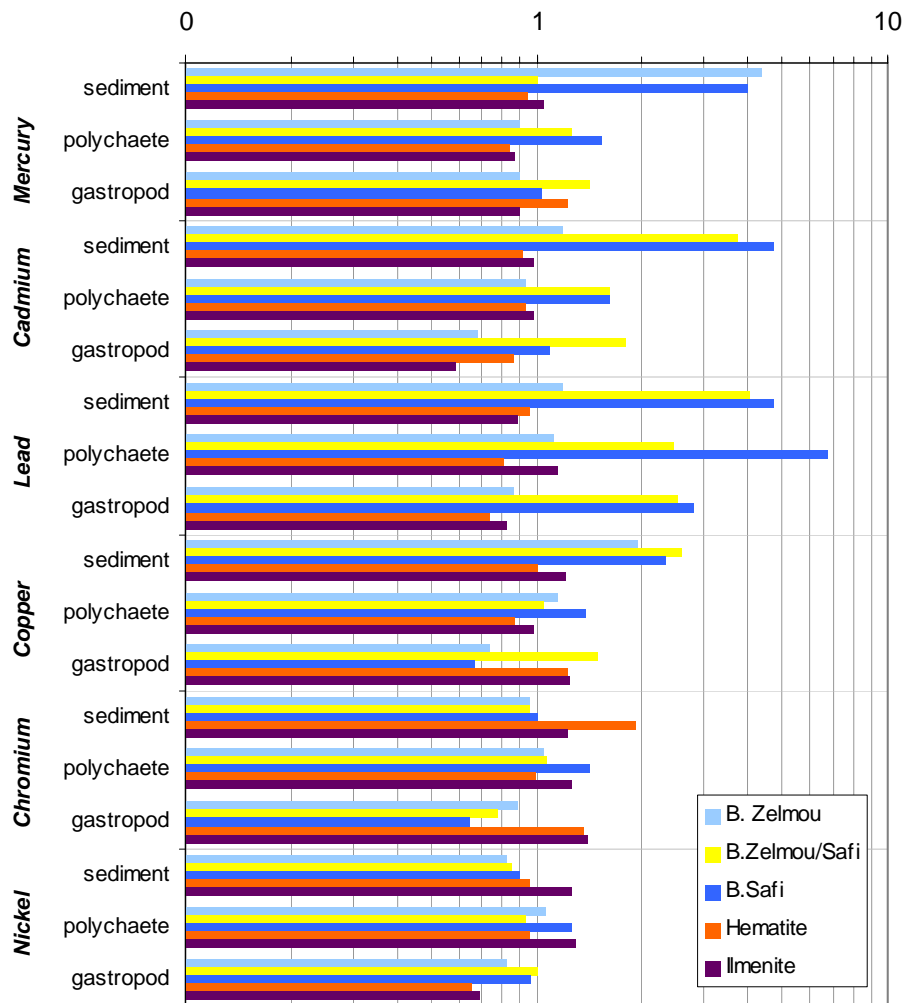


Figure 5. Metal enrichment ratios (SER and BAR for Hg, Cd, Pb, Cu, Cr and Ni) in organisms after 28 days exposure in control sediments or sediments spiked with test substances.

4.2.2 Fe

In spite of the high concentration of Fe in the Ilmenite and Hematite test substances, Fe did only show up as a consistent enrichment in the Hematite sediments (SER = 1,28) and organisms (BAR = 1,30 and 1,40). The insolubility of these Fe-minerals in nitric acid was discussed in the previous chapter, and it appears likely that total dissolution in hydrofluoric acid would have revealed more strongly elevated Fe-ratios in sediments as well as in biological samples from the Hematite and Ilmenite samples.

4.2.3 Zn

The elevated SER ratios of 1,63 and 1,51 for Zn in sediment samples from Barite Zelmou/Safi and Barite Safi was consistent with the concentrations in the test substances, but none of the biological samples exceeded a BAR ratio of 1,18.

4.2.4 Ba

Not only the Barites, but also the Ilmenite and Hematite test substances were enriched with Ba relative to control sediments (Table 1) and all test substances yielded high sediment enrichment ratios (5-137) (Table 3). The sediment enrichment ratios for the three Barite test substances were approximately one order of magnitude higher than any other bioaccumulation ratio obtained in the present test, and only the three Barite treatments gave elevated bioaccumulation ratios for Ba (Table 3). These ranged 25-75 in the gastropode samples and 66-259 in the polychaete samples. The bioaccumulation ratios were significantly larger than 1,00 in all biological samples from the Barite treatments.

4.2.5 Ti

Titanium is not an important element in barites, and this element was therefore omitted in the analyses of Barite Safi and Barite Zelmou/Safi. In the Hematite and Barite Zelmou treatments, sediment enrichment and bioaccumulation ratios ranged between 0,78 and 1,19. For Ilmenite the SER was 1,4 (Table 3), and the BARs were 5,66 for the polychaetes and 2,16 for the gastropodes. Compared to the high concentration in the test substance, these ratios were not as high as one might expect and it should not be ruled out that both sediment and test organisms may have contained considerable fractions of Ti not soluble in nitric acid. The BARs for Ti were significantly larger than 1,00 for both test organisms exposed to Ilmenite.

4.2.6 Hg

The concentrations of mercury were low in the Ilmenite and Hematite substances and the sediment enrichment and bioaccumulation ratios ranged between 0,83 and 1,23. The Barite test substances, however, were up to “markedly polluted” (Table 1) and the SERs ranged 1,68-6,72. Both BAR ratios for the organisms exposed to Barite Zelmou/Safi were significantly $>1,0$ at the 95% significance level.

4.2.7 Cr

The Barite test substances contained little of this element and disregarding the sediment contaminated polychaete sample, the sediment enrichment and bioaccumulation ratios were low (range 0,65-1,13). The Hematite and Ilmenite test substances were moderately to markedly polluted with Cr, but as shown in Table 1, a large fraction of the Cr present in Ilmenite in particular, appeared insoluble in nitric acid. Three of the four bioaccumulation ratios were slightly elevated (1,26-1,40) indicating some bioaccumulation, but none of the ratios were significantly $>1,0$ at the 95% significance level.

4.2.8 Ni

The concentration of Ni was high (147 mg/kg) in the Ilmenite test substance as compared to 3-10 mg/kg in all other test substances (Table 1). Disregarding the sediment contaminated Barite Safi polychaete sample, all SER and BAR ratios for hematite and barite treatments ranged between 0,66 and 1,05. For Ilmenite, the sediment enrichment ratio of 1,26 and polychaete bioaccumulation ratio of 1,29 was high compared to the other Ni-ratios, but not significantly $>1,0$ at the 95% significance level. Neither did the gastropode ratio of 0,69 yield any supporting evidence for bioaccumulation of Ni. Gastropodes are however, known to be able to regulate their contents of some metals, and the possibility exists that the low Ni bioaccumulation ratio in the gastropodes exposed to Ilmenite was a result of such processes.

4.2.9 Cu

The test substances had rather variable concentrations of Cu. Hematite had the lowest content followed by Ilmenite, Barite Zelmou, Barite Safi and Barite Zelmou/Safi. The sediment enrichment ratios shown in Table 3 followed the same order, but the bioaccumulation ratios did not. Apart from the Barite Safi polychaete samples, the polychaete BARs were consistently low ranging 0,88-1,15. The gastropode bioaccumulations ratios varied more strongly from 0,67 in Barite Safi to 1,49 (significantly > 1,0) in Barite Zelmou/Safi. Gastropodes are however, known to be able to regulate the bioaccumulation of copper and is not considered a good indicator on this metal.

4.3 Evaluation of test results

4.3.1 Evidence for bioaccumulation

The results on Al and Li showed that the rinsing of sediment particles from guts and body extensions had been acceptable to the extent that only one of the biological samples were clearly contaminated with sediment. The evaluation is based on the corrected value (ref. ch. 4.2.1) for this sample.

Bioaccumulation ratios which were significantly larger than 1,0 (at $p < 0,05$), were found for

- Ti in both test species exposed to Ilmenite,
- Ba in both test species exposed to all types of Barite,
- Pb in both test species exposed to Barite Zelmou Safi and Barite Safi,
- Hg in both test species exposed to Barite Zelmou/Safi, and
- Cu in gastropodes exposed to Barite Zelmou/Safi.

Other evidence for bioaccumulation was found from consistence between elevated concentrations in test substances, elevated sediment enrichment ratios (SERs) and elevated bioaccumulation ratios (BAR 1,24) for both polychaetes and gastropods. Such evidence for bioaccumulation was found for:

- Fe from Hematite,
- Cd from Barite Zelmou/Safi and
- Cr from Ilmenite.

Yet weaker evidence based on elevated concentrations in test substances and elevated bioaccumulation ratios (BAR 1,24) in either polychaetes or gastropods were found for

- Fe in polychaetes exposed to Ilmenite,
- Ba in gastropodes exposed to Hematite,
- Cd and Hg in polychaetes exposed to Barite Safi,
- Cu in gastropodes exposed to Ilmenite
- Cr in gastropodes exposed to Hematite and
- Ni in polychaetes exposed to Ilmenite.

Table 4. Test substance classification (insignificantly, moderately or markedly polluted, after Molvær et al., 1997) and observations of bioaccumulation ratios 1,24 in gastropodes (G) and polychaetes (P). Classification criteria are not defined for Fe, Ti and Ba. Asterix (*) shows significant bioaccumulation ($p < 0,05$).

	Fe	Ti	Ba	Hg	Cd	Cr	Cu	Ni	Pb	Zn
Barite Zelmou			P*G*							
Hematite	PG		G			G				
Ilmenite	P	P*G*				PG	G	P		
Barite Safi	P		P*G*	P	P				P*G*	
Barite Zelmou/Safi			P*G*	P*G*	PG		G*#		P*G*	

#Gastropodes may regulate bioaccumulation of copper.

The various evidence for bioaccumulation found in the present study is summarised in Table 4 which shows a P (polychaete) or a G (gastropode) for all observations of BAR 1,24. The boundary criterion BAR 1,24 was chosen after careful consideration of all ratios given in Table 3 and the concentrations of metals observed in the test substances. Clearly the ratio of 1,26 for Hg in polychaetes exposed to Barite Zelmou/Safi should be included because it was significantly higher than 1,0 and consistent with elevated SER and gastropode BAR. On the other hand two ratios of 1,23 (Hg and Cu in gastropodes exposed to Hematite) were omitted because of the lack of support by other observations.

4.3.2 Rank of test substances

Ranking the least harmful weight substance should not be done without considering both the magnitude of the bioaccumulation ratios and the toxicity of the metals involved. Thus, high bioaccumulation of low-toxic components such as iron in Hematite, iron and titanium in Ilmenite and barium in Barite, may contribute less to test substance toxicity than low bioaccumulation of the heavy metals (Hg, Cd, Pb, Cu, Cr and Ni).

Weighting the evidence for bioaccumulation of iron, titanium and ilmenite

From test substance analyses using hydrofluoric acid for complete dissolution, enrichment ratios for iron in sediments spiked with Hematite and Ilmenite and for titanium in sediments spiked with Ilmenite should not be very different from the ratios for barium in sediments spiked with barite. As shown in ch.4.1 and Table 1, incomplete dissolution of Hematite and Ilmenite in the nitric acid used in analyses of test sediments (and biological tissues) gave sediment enrichment ratios much lower than calculated from test substance analyses for iron in sediments spiked with Hematite (observed 1,3 vs calculated 4,7) or Ilmenite (observed 1,0 vs calculated 6,9) and for titanium in sediments spiked with Ilmenite (observed 1,4 vs calculated 89,9). Barite may be incompletely dissolved in either method and observed sediment enrichment ratios of 124-137 were spuriously high compared to the ratios between 40,4 and 43,6 calculated from the analyses of the test substances. Because of the obvious analytical difficulties, care should be taken when evaluating the different magnitudes between the high bioaccumulation ratios observed for barium in the barites and the lower ratios observed for e.g. titanium in Ilmenite.

Uptake of dissolved ions are generally considered more harmful than uptake via phagocytosis of mineral particles. Solubility of barium and titanium is low in marine waters, but evidence has been found for mobilisation of both barium (McManus et al., 1998) and titanium (Skrabal et al., 2002) in pore waters of low-oxic carbon-enriched marine sediments. Pore water concentrations and fluxes from sediments to the overlying seawater were frequently 10-100x higher for barium (100-400 nM, 27-56 nmol cm⁻² y⁻¹) than for titanium (4-80 nM, 0,1-3 nmol cm⁻² y⁻¹). Even though these fluxes are rather low, the pore water pathway for uptake of Ba and Ti should not be entirely disregarded.

Comparison of bioaccumulation ratios (BAR) and sediment enrichment ratios (SER) may yield some further indications on uptake mechanisms. If BAR<SER, bioaccumulation may be fully explained by non-selective uptake of sediment particles. If BAR>SER, selective uptake via dissolved ions or phagocytosis of e.g. very small mineral particles appears to be involved. As shown in Table 3 bioaccumulation ratios for barium were frequently smaller than sediment enrichment ratios

Table 5. BAR/SER ratios for Al- and Li-normalised barium concentrations in barite treatments and titanium concentrations in Ilmenite treatments ($BAR_{Ba(Ti):Al(Li)}/SER_{Ba(Ti):Al(Li)}$).

	Barite		Ilmenite	
	Ba:Al	Ba:Li	Ti:Al	Ti:Li
Polychaetes	0,56	0,92	2,68	3,48
Gastropodes	0,24	0,27	1,79	1,50

(BAR<SER), whereas the opposite (BAR>SER) was found for titanium. This is shown more clearly in

Table 5, which shows BAR/SER ratios calculated from Al- and Ti-normalised concentrations of Ba in barium treatments and Ti in Ilmenite treatments. The normalisation means that the concentration of Ba (C_{Ba}) and Ti (C_{Ti}) in both sediments and organisms were replaced with the concentration ratios (C_{Ba}/C_{Al} , C_{Ba}/C_{Li} , C_{Ti}/C_{Al} and C_{Ti}/C_{Li}).

Thus, some evidence was found that titanium is taken up selectively, possibly via phagocytosis of small mineral particles. Barium showed no indications on selective uptake. Furthermore, titanium may be more strongly underestimated than barium due to low yields of nitric acid extractions. Eitherway toxic effects of titanium or solid phase barium are not known.

Ranking the least harmful weight materials

Ranking the least harmful weight material was therefore based primarily on the evidence found for bioaccumulation of the more toxic heavy metals Hg, Cd, Cr, Cu, Ni, Pb and Zn.

Barite Zelmou showed no evidence for bioaccumulation of any other metal than barium. Hematite yielded weak evidence for bioaccumulation of iron, barium and chromium. These two must be ranked clearly before Ilmenite which in addition to significant bioaccumulation of titanium, showed some evidence for bioaccumulation of iron, chromium, copper and nickel. Because of the evidence for bioaccumulation in Hematite this test substance may be ranked slightly behind the Barite Zelmou.

The Barite Safi and the Barite Zelmou/Safi showed significant bioaccumulation of barium and occasionally significant bioaccumulation of lead, mercury, cadmium and copper. Both must be ranked behind Ilmenite. Even though the analyses of the test substances showed that Barite Safi had higher concentrations of Hg and Cd than Barite Zelmou/Safi, the Barite Safi yielded less evidence on bioaccumulation and was therefore ranked before Barite Zelmou/Safi.

5. Conclusion

Bioaccumulation ratios significantly larger than 1,0 were found for Ba in all barite types and for Pb, Hg and Cu in organisms exposed to sediments spiked with Barite Safi or Barite Zelmou/Safi. In addition, weaker evidence was found for bioaccumulation of Cd from the two latter barite types.

Bioaccumulation ratios significantly larger than 1,0 were also found for Ti in organisms exposed to sediments spiked with Ilmenite and weaker evidence were found for bioaccumulation of Cr, Cu, Ni and Fe from this test substance.

No significant evidence was found on bioaccumulation of metals from Hematite, but some weaker evidence was found for bioaccumulation of Fe, Ba and Cr.

Apart from the absence of any evidence for bioaccumulation of Zn, elevated bioaccumulation ratios were in general consistent with elevated concentrations of metals in the test substance.

Based on the present test results, Hematite and Barite Zelmou appears to be the least harmful weight substances. The difference between these two test products was small, but because of the absence of any evidence for bioaccumulation of neither Hg, Cd, Cr, Cu, Ni, Pb or Zn, Barite Zelmou may be ranked slightly before Hematite.

Significant evidence for bioaccumulation of more toxic metals like Pb and Hg ranked Barite Safi and Barite Zelmou/Safi behind the other test substances. Barite Safi came out slightly better than Barite Zelmou/Safi, but the difference was small between these two products.

The evidence found for bioaccumulation of Pb, Hg and Cd from Barite Safi and Zelmou/Safi tend to confirm previous findings from field and experimental studies. Bioaccumulation of Cu from barites have not been found in previous works, and the present evidence on bioaccumulation in gastropodes exposed to Barite Zelmou/Safi may have been biased from active regulation of copper in gastropodes. Previously reported bioaccumulation of Zn was not confirmed in this study.

Even though major mineral components such as Ba, Fe or Ti or impurities such as Pb, Hg, Cd, Cu, Cr and Ni may be taken up in sediment dwelling animals, harmful effects on marine, benthic communities are difficult to distinguish from effects provoked by other mud components. Mesocosm experiments on soft bottom communities as well recent toxicity tests of off-shore sediment samples both conclude that organic phases are the most significant cause of adverse effects in areas contaminated with drilling muds. One study has related inhibited enzyme activity in turbot to uptake of lead after exposure to barite with high concentrations of lead, but evidence of adverse effects from metals in drill cuttings is scarcely found in the scientific literature.

6. References

- Bakke, T., Green, N.W., Naes, K., and Pedersen, A., 1986. Drill cuttings on the sea bed. Phase 1 and 2. Field experiment on the benthic recolonization and chemical changes in response to various types and amounts of cuttings. In: *Oil based drilling fluids. Cleaning and environmental effects of oil contaminated drill cuttings. Proceedings*. Norsk Petroleumsforbund, Trondheim, pp 17-31.
- Barlow, M.J. and Kingston, P.F. (2001) Observations on the Effects of Barite on the Gill Tissues of the Suspension Feeder *Cerastoderma edule* (Linne) and the Deposit Feeder *Macoma balthica* (Linne). *Mar.Pollut.Bull.* 42, 71-76.
- Burke CJ, Veil JA. 1995. Synthetic-based drilling fluids have many environmental pluses. *Oil Gas J.* 93: 59-71.
- Carls, M.G. and Rice, S.D. (1984) Toxic contributions of specific drilling mud components to larval shrimp and crabs. *Mar.environ.Res.* 12, 45-62.
- Chapman PM. 1992. Pollution status of North Sea sediments – an international integrative study. *Mar. Ecol. Prog. Ser.* 91: 313-322.
- Clark, J.R. and Patrick, J.J. (1987) Toxicity of sediment-incorporated drilling fluids. *Mar.Pollut.Bull.* 18, 600-602.
- Colwell, C.S., Michel, S. and Block, G.D. (1992) Evidence that potassium channels mediate the effects of serotonin on the ocular circadian pacemaker of *Aplysia*. *Journal of Comparative Physiology* 171, 651-656.
- Cranford, P.J., Gordon, D.J., Lee, K., Armsworthy, S.L. and Tremblay, G.H. (1999) Chronic toxicity and physical disturbance effects of water- and oil-based drilling fluids and some major constituents on adult sea scallops (*Placopecten magellanicus*). *Mar.environ.Res.* 48, 225-256.
- Daan, R., K.Booij, M.Mulder and E.M. van Weerle, 1996. Environmental Effects of a Discharge of Drill Cuttings Contaminated with Ester-based Drilling Muds in the North Sea. *Environmental Toxicology and Chemistry*, Vol. 15, No. 10, pp. 1709-1722.
- Davies JM, Addy JM, Blackman RA, Blanchard JR, Ferbrache JE, Moore DC, Somerville HJ, Whitehead A, Wilkinson T. 1984. Environmental effects of the use of oil-based drilling muds in the North Sea. *Mar. Pollut. Bull.* 15: 363-370.
- E&P Forum 1996. The physical and biological effects of processed oily drill cuttings (Summary Report). E&P Forum Report No. 2.61/202. 114 pp.
- ERT (scotland) ltd., 2001. Investigation of the toxicokinetics of water based mud cuttings Draft final report. ERTSL Report No 00/228 to UKOOA JIP. 27 pp.
- Farestveit, R., Hylland, K. and Haaland, H. (1994) Biologisk tilgjengelighet av tungmetaller i baritt og ilmenitt. pp.1-35. Trondheim: Statoil. [in Norwegian]

- Fjogstad A., A.Saasen, R.Hagen, P.B.Tanche-Larsen, R.Ree, H.Melgren, E.Rostad and H.Hoset, 2000. Field Trial of Alternative Weight Material with Improved Occupational Hygiene and Environmental Performance. *SPE conference Stavanger Norway 26-28 June 2000*, SPE 61042, 8 pp.
- Fjogstad A., P.B.Tanche-Larsen, M.Løkken and R.James, 2002. It's Not Your Grandfather's Ilmenite. Drilling and Completion Fluids and Waste Management. Houston, Texas, April 2-3, 2002. AADE-02-DFWM-HO-40. 9 pp.
- Fowler SW, Polikarpow GG, Elder DL, Parsi P, Villeneuve JP. 1978. Polychlorinated biphenyls: accumulation from contaminated sediments and water by the polychaete *Nereis diversicolor*. *Mar Biol* 48:303-309.
- Goerke H. 1971. Die Ernährungsweise der Nereis-Arten (Polychaeta, Nereidae) der deutschen Küsten. *Veröff Inst Meeresforsch Bremerh* 13:1-50.
- Goerke H. 1984. Testing the fate of xenobiotics in *Nereis diversicolor* and *Nereis virens* (Polychaeta). In G Persoone, E Jaspers & C Claus (Eds.), *Ecotoxicological testing for the marine environment*. pp 53-66.
- Grant A. and A.D. Briggs. 2002. Toxicity of sediments from around a North Sea oil platform: are metals or hydrocarbons responsible for ecological impacts? *Mar. Envir. Res.* 53: 95-113.
- Gray JS, Clarke KR, Warwick RM, Hobbs G. 1990. Detection of initial effects of pollution on marine benthos: an example from the Ekofisk and Eldfisk oilfields, North Sea. *Mar. Ecol. Prog. Ser.* 66: 285-299.
- Hamano, S., Morita, K., Azuma, M., Oka, M. and Teraoka, K. (1991) Pharmacological study on Ba²⁺-stimulated catecholamine secretion from cultured bovine adrenal chromaffin cells: possible relation of Ba²⁺ action to Ca²⁺-activated secretory mechanism. *Jpn J Pharmacol* **55**, 43-50.
- Hamilton, P.V., Winter, M.A. and Pegg, R.K. (1981) Effects of whole drilling mud and selected components on the shell movements of the bay scallop, *Argopecten irradians*. *Northeast Gulf Sci.* **5**, 13-20.
- Haux, C., Larsson, Å., Lithner, G. and Sjöbeck, M.-L. (1986) A field study of physiological effects on fish in lead- contaminated lakes. *Environ.Toxicol.Chem.* **5**, 283-288.
- Hodson, P.V. (1976) δ -amino levulinic acid dehydratase activity of fish blood as an indicator of a harmful exposure to lead. *J.Fish.Res.Board Can.* **33**, 268-271.
- Hodson, P.V. (1988) The effect of metal metabolism on uptake, disposition and toxicity in fish. *Aquat.Toxicol.* **11**, 3-18.
- Hodson, P.V., Blunt, B.R., Spry, D.J. and Austen, K. (1977) Evaluation of erythrocyte δ -amino levulinic acid dehydratase activity as a short-term indicator in fish of a harmful exposure to lead. *J.Fish.Res.Board Can.* **34**, 501-508.
- Hogstrand, C. and Haux, C. (1991) Binding and detoxification of heavy metals in lower vertebrates with reference to metallothionein. *Comp.Biochem.Physiol.* **100C**, 137-142.

- Holdway DA. 2002. The acute and chronic effects of wastes associated with offshore oil and gas production on temperate and tropical marine ecological processes. *Mar. Pollut. Bull.* 44: 185-203.
- Hyland, J., D.Hardin, M.Steinbauer, D.Coats, R.Green and J.Neff, 1994. Environmental Impact of Offshore Oil Development on the Outer Continental Shelf and Slope off Point Arguello, California. *Marine Environmental Research* 37, 195-229.
- Hylland, K. (1993) Effekter av baritt- og ilmenitt-anriktet fôr på piggvar. pp.1-15. Oslo: *Universitetet i Oslo*. [in Norwegian]
- Hylland, K., Sköld, M., Gunnarsson, J. and Skei, J. (1996) Interactions between eutrophication and contaminants. IV. Effects on sediment-dwelling organisms. *Mar.Pollut.Bull.* 33, 90-99.
- Hylland K. 1996. Bioakkumulering av miljøgifter fra marine sediment – etablering av et test-system. *NIVA-rapport* Inr 3537.
- Isotalo, T., Alarakkola, E., Talja, M., Tammela, T.L., Valimaa, T. and Tormala, P. (1999) Biocompatibility testing of a new bioabsorbable X-ray positive SR-PLA 96/4 urethral stent. *J Urol* 162, 1764-1767.
- Jensen T, Palerud R, Olsgard F, Bakke SM. 1999. Dispersion and effects of synthetic drilling-muds in the environment. Draft report for the Norwegian Ministry of Petroleum and Industry. (In Norwegian).
- Johansson-Sjöbeck, M.-L. and Larsson, Å. (1979) Effects of inorganic lead on delta-aminolevulinic acid dehydratase activity and hematological variables in the rainbow trout, *Salmo gairdnerii*. *Arch.Environ.Contam.Toxicol.* 8, 419-431.
- Johnsen TM, Schaanning M, Hylland K. 1996. Kobberbelastning i forbindelse med vasking og impregnering av fiskenøter. *NIVA-rapport* Inr 3483.
- Kingston PF. 1992. Impact of offshore oil production installations on the benthos of the North Sea. *ICES J. Mar. Sci.* 49: 45-53.
- Knutzen J, Skei J, Johnsen TM, Hylland K, Klungsøyr J, Schlabach M. 1995. Miljøgiftundersøkelser i Byfjorden/Bergen og tiliggende fjordområder. Fase 2. Observasjoner i 1994. *NIVA-rapport* Inr 3351.
- Kopp, S.J., Perry, H.M., Feliksik, J.M., Erlanger, M. and Perry, E.F. (1985) Cardiovascular dysfunction and hypersensitivity to sodium pentobarbital induced by chronic barium chloride ingestion. *Toxicol.appl.Pharmacol.* 77, 303-314.
- Krajnovic-Ozretic, M. and Ozretic, B. (1980) The ALA-D activity test in lead-exposed grey mullet *Mugil cephalus*. *Mar.Ecol.prog.Ser.* 3, 187-191.
- Lee H, Boese BL, Pelletier J, Winsor M, Specht DT, Randall RC. 1991. Guidance manual: bedded sediment bioaccumulation tests. EPA/600/x-89/302.
- Leuterman, A., I.Still, I.Johnson, J.Christie and N.Butcher. 1997. A Study of Trace Metals from Barites: Their Concentration, Bioavailability and Potential for Bioaccumulation. Offshore Mediterranean Conference OMC97, 357-369.

- Loring D.H. and R.T.T. Rantala, 1989: *Anal. Chim. Acta*, 220, 263-7.
- McManus, J., W.M.Berelson, G.P.Klinkhammer, K.S.Johnson, K.H.Coale, R.F.Anderson, N.Kumar, D.J.Burdige, D.E.Hammond, H.J.Brumsack, D.C.McCorkle and A.Rushdi, 1998. Geochemistry of barium in marine sediments: Implications for its use as a paleoproxy. *Geochimica et Cosmochimica Acta*, Vol. 62, No. 21/22, pp.3453-3473.
- Molvær, J., J.Knutzen, J.Magnusson, B.Rygg, J.Skei og J.Sørensen, 1997. Klassifisering av miljøkvalitet i fjorder og kystfarvann. Veiledning. SFT TA-1467/1997. 36s.
- Newman, E.A. (1989) Potassium conductance block by barium in amphibian Mueller cells. *Brain Research* 498, 308-314.
- NS 4770, Norsk Standard, Metaller i vann, slam og sedimenter. Bestemmelse ved atomabsorpsjonsspektrofotometri i flamme. Generelle prinsipper og retningslinjer. 2. Utg. 1994.
- Olsgard F. and J.S.Gray. 1995. A comprehensive analysis of the effects of offshore oil and gas exploration and production on the benthic communities of the Norwegian continental shelf. *Mar. Ecol. Prog. Ser.* 122: 277-306.
- Oug E, Olsgard F, Ruus A, Skei J and Rygg B. 2002. Risk assessment related to contaminated sediments – with focus on Kristiansandsfjorden. Norwegian Pollution Control Authority report 1864/2002.
- Ruus A. 2001. Disposition of organochlorine contaminants within marine food webs. Dr. scient. thesis. *Universitetet i Oslo*.
- Prasad, P.V.D. (1984) Effect of magnesium, strontium and barium on the calcification of the freshwater green alga *Gloeotaenium*. *Phykos (Algiers) [PHYKOS.]* **23**, 202-206.
- Schaanning, M., 1995. Biodegradation of Ultidril Base Fluid and Drilling Mud on Cuttings Deposited in Benthic Chambers. NIVA report no. 3321. 64pp+appendix.
- Schaanning, M., 1996. Environmental Fate of Synthetic Drilling Fluids from Offshore Drilling Operations - An Experimental Study of an Olefin-, Ether- and Ester-Based Mud System on Cuttings Deposited in Benthic Chambers. *NIVA Report 3429*. 55pp + appendix.
- Schaanning, M., Hylland, K., Lichtenthaler, R., Rygg, B. (1996) Biodegradation of *Anco Green* and *Novaplus* Drilling Muds on Cuttings Deposited in Benthic Chambers. *NIVA-report 3475-96*, 77 p + appendices.
- Schaanning, M. and T.Bakke, 1997. Environmental fate of drill cuttings in mesocosm and field. *SEBA, UK National Workshop on Drilling Fluids*, Aberdeen 11-14.November 1997. WDF97/3/6, 10pp.
- Schmitt, C.J., Dwyer, F.J. and Finger, S.E. (1984) Bioavailability of Pb and Zn from mine tailings as indicated by erythrocyte δ -aminolevulinic acid dehydratase (ALA-D) activity in suckers (Pisces: Catostomidae). *Can.J.Fish.aquat.Sci.* **41**, 1030-1040.
- Skei J, Andersen L. 1996. Nedbryting av DDT i sedimenter og bioakkumulering i sedimentlevende dyr. NIVA-rapport lnr 3531.

- Skrabal, S.A. and C.M.Terry, 2002. Distributions of dissolved titanium in porewaters of estuarine and coastal marine sediments. *Mar. Chem.* 77, pp. 109-122.
- Smith, G.A., Nickels, J.S., Bobbie, R.J., Richards, N.L. and White, D.C. (1982) Effects of Oil and Gas Well-Drilling Fluids on the Biomass and Community Structure of Microbiota That Colonize Sands in Running Seawater. *Arch. Environ. Contam. Toxicol.* 11, 17-23.
- Saasen, A., H.Hoset, E.J.Rostad, A.Fjogstad, O.Aunan, E.Westgård and P.I.Norkyn, 2001. Application of Ilmenite as weight Material in Water Based and Oil Based Drilling Fluids. Society of Petroleum Engineers, New Orleans 30.09.-03.10.2001. SPE 71401. 5 pp.
- Tagatz, M.E. and M.Tobia, 1978. Effect of Barite (BaSO₄) on Development of Estuarine Communities. *Estuarine and Coastal Marine Science* 7, 401-407.
- Triadafilopoulos, G., Tsang, H.P. and Segall, G.M. (1998) Hot water swallows improve symptoms and accelerate esophageal clearance in esophageal motility disorders. *J Clin Gastroenterol.* 26, 239-244.
- UKOOA, 2001. UKOOA drill cuttings initiative. Final report. United Kingdom Offshore Operators Association December 2001. 58 pp.
- URS Dames and Moore, and TNO, 2001. UKOOA Drill Cutting Initiative Joint Industry Project, Research & Development Programme Phase II Task 2C Water Column and Food Chain Impacts. Final Draft. URS and TNO report ref 29384-010-401. 73 pp.
- van Driessche, W. and Wolf, I. (1991) Microelectrode study of voltage-dependent Ba super(2+) and Cs super(+) block of apical K super(+) channels in the skin of *Rana temporaria*. *Pfluegers Archiv/European Journal of Physiology [PFLUEGERS ARCH.* 418, 400-407.
- Westerlund, S., Eriksen, V., Beyer, J., and Keilen, G., 2001. Characterisation of the cuttings piles at the Beryl A and Ekofisk 2/4 A platform - UKOOA Phase II, task 1. Rogaland Research Report No. RF 2001/092, 162 pp.

Appendix A. Analyses in organisms

Table 6. Metal analyses in organisms ($\mu\text{g/g}$ wet wght.).

Organism	Treatment	Al	Ba	Cd	Cr	Cu	Fe	Hg	Li	Ni	Pb	Ti	Zn
Gastropode	Barite Safi	161	489	1,690	0,56	26,5	303	0,022	0,27	0,488	0,553	na	123,0
Gastropode	Barite Safi	91	256	0,541	0,41	14,4	225	0,015	0,15	0,499	0,420	na	89,6
Gastropode	Barite Safi	198	661	0,346	0,75	12,4	369	0,016	0,28	0,666	1,080	na	42,7
Gastropode	B. Zelmou	100	216	0,285	0,32	19,0	293	0,027	0,24	2,240	0,219	33,9	69,0
Gastropode	B. Zelmou	89	280	0,490	0,28	17,9	300	0,028	0,22	1,150	0,211	21,0	79,7
Gastropode	B. Zelmou	51	131	1,270	0,16	29,5	229	0,043	0,18	0,790	0,179	14,9	143,0
Gastropode	B. Zelmou/Safi	167	663	0,708	0,72	34,1	272	0,022	0,25	0,780	0,555	na	68,7
Gastropode	B. Zelmou/Safi	212	804	2,570	0,79	56,0	446	0,029	0,29	0,514	0,899	na	161,0
Gastropode	B. Zelmou/Safi	120	407	0,949	0,54	28,0	252	0,021	0,19	0,425	0,401	na	72,6
Gastropode	Control I	111	2,21	1,690	0,40	49,0	377	0,047	0,26	1,170	0,268	17,0	167,0
Gastropode	Control I	90	4,85	0,834	0,15	30,3	282	0,034	0,23	2,130	0,205	21,5	152,0
Gastropode	Control I	119	1,25	0,473	0,31	11,1	336	0,029	0,27	1,760	0,239	22,1	68,2
Gastropode	Control II	71	23,4	0,685	0,93	25,7	236	0,018	0,17	0,260	0,294	na	77,8
Gastropode	Control II	140	21	1,150	0,82	27,0	265	0,019	0,20	0,839	0,199	na	116,0
Gastropode	Control II	196	10,8	0,534	0,91	26,5	325	0,014	0,29	0,616	0,243	na	89,5
Gastropode	Hematite	73	3,48	0,879	0,41	54,2	429	0,048	0,18	1,140	0,198	22,2	163,0
Gastropode	Hematite	55	3,19	0,807	0,31	18,6	335	0,039	0,14	0,677	0,143	18,1	114,0
Gastropode	Hematite	87	5,54	0,877	0,45	38,1	525	0,048	0,21	1,500	0,180	16,8	97,5
Gastropode	Ilmenite	88	1,77	0,616	0,34	42,2	318	0,030	0,21	1,200	0,189	42,6	81,3
Gastropode	Ilmenite	91	1,96	0,393	0,37	25,1	349	0,034	0,21	1,340	0,194	44,5	81,9
Gastropode	Ilmenite	117	2,72	0,748	0,49	44,5	381	0,034	0,24	0,949	0,204	46,3	176,0
Polychaete	Barite Safi	47	342	0,011	0,53	3,4	125	0,008	0,14	0,236	0,231	na	22,0
Polychaete	Barite Safi	102	864	0,024	0,72	3,1	201	0,012	0,21	0,317	0,629	na	20,0
Polychaete	Barite Safi	48	370	0,015	0,35	2,2	109	0,009	0,15	0,239	0,264	na	15,0
Polychaete	B. Zelmou	15	70,5	0,012	0,28	2,1	79	0,010	0,14	0,415	0,080	1,6	18,1
Polychaete	B. Zelmou	19	86,7	0,012	0,28	2,1	85	0,009	0,15	0,385	0,064	1,9	13,1
Polychaete	B. Zelmou	51	329	0,013	0,45	2,1	154	0,008	0,19	0,376	0,092	4,5	16,4
Polychaete	B. Zelmou/Safi	18	149	0,015	0,54	2,1	70	0,008	0,12	0,178	0,114	na	13,8
Polychaete	B. Zelmou/Safi	22	161	0,020	0,35	2,2	86	0,008	0,12	0,192	0,164	na	19,5
Polychaete	B. Zelmou/Safi	24	161	0,015	0,33	2,3	98	0,008	0,12	0,217	0,132	na	17,1
Polychaete	Control I	26	3,06	0,013	0,28	1,4	92	0,007	0,17	0,343	0,069	2,7	16,3
Polychaete	Control I	20	2,65	0,011	0,42	2,0	88	0,012	0,23	0,495	0,066	2,1	16,6
Polychaete	Control I	17	1,58	0,016	0,27	2,1	99	0,011	0,14	0,277	0,078	1,9	18,5
Polychaete	Control II	5	1,66	0,006	0,38	2,3	49	0,005	0,13	0,173	0,038	na	14,0
Polychaete	Control II	41	0,72	0,010	0,40	2,1	104	0,007	0,13	0,215	0,058	na	17,7
Polychaete	Control II	31	2,22	0,015	0,35	1,9	94	0,007	0,13	0,245	0,071	na	16,6
Polychaete	Hematite	12	2,88	0,013	0,33	1,5	123	0,007	0,13	0,410	0,083	1,6	20,5
Polychaete	Hematite	5	0,485	0,012	0,24	1,5	82	0,009	0,14	0,334	0,039	0,9	17,8
Polychaete	Hematite	22	2,15	0,012	0,39	1,7	182	0,009	0,15	0,318	0,051	2,7	16,0
Polychaete	Ilmenite	8	0,279	0,011	0,28	1,5	78	0,007	0,13	0,431	0,042	4,2	16,2
Polychaete	Ilmenite	77	6,05	0,012	0,62	1,8	241	0,008	0,22	0,615	0,146	27,2	17,7
Polychaete	Ilmenite	14	0,577	0,016	0,32	2,1	87	0,011	0,13	0,397	0,058	6,5	23,5

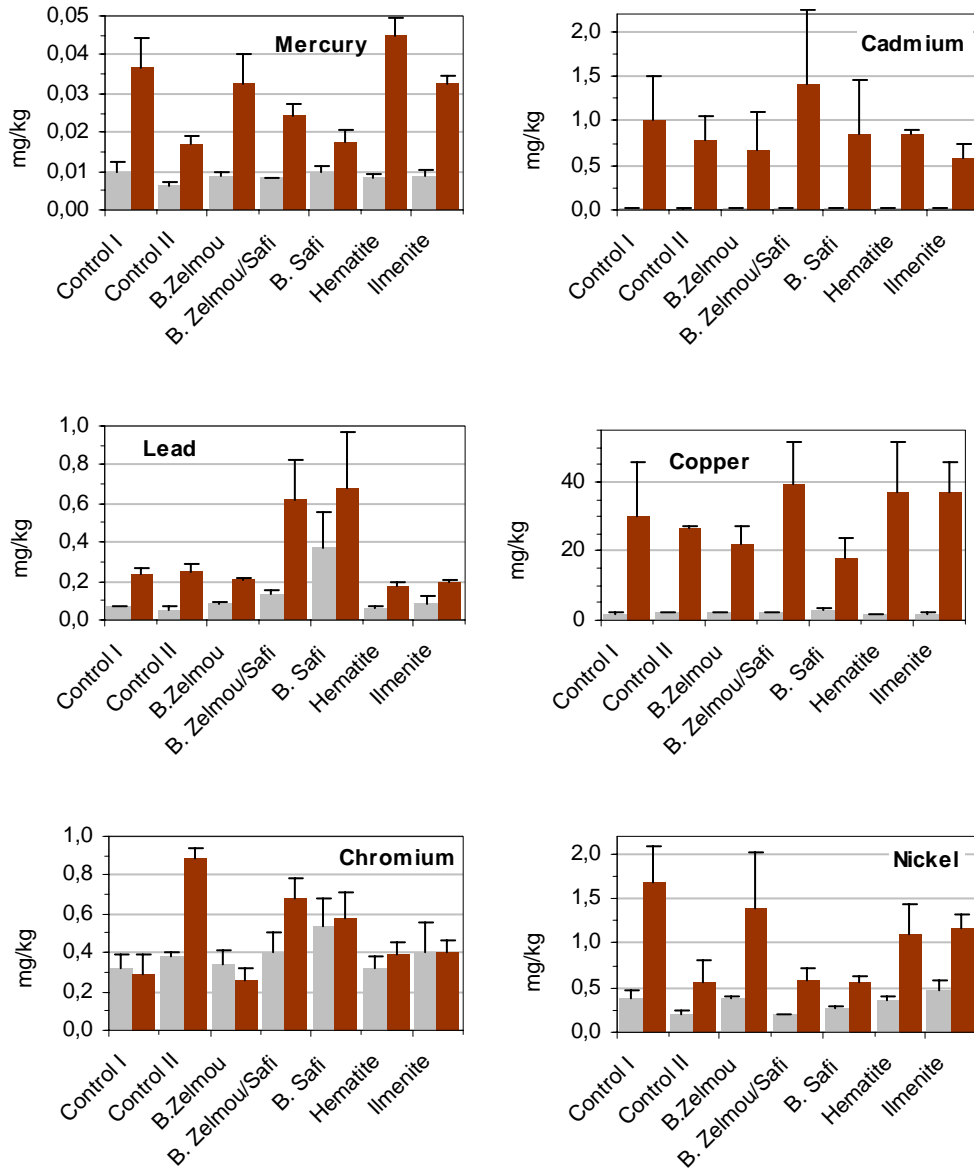


Figure 6. Mean concentration of metals (Hg, Cd, Pb, Cu, Cr and Ni) in organisms after 28 days exposure in control sediments or sediments spiked with test substances. Error bars = 1 standard deviation.

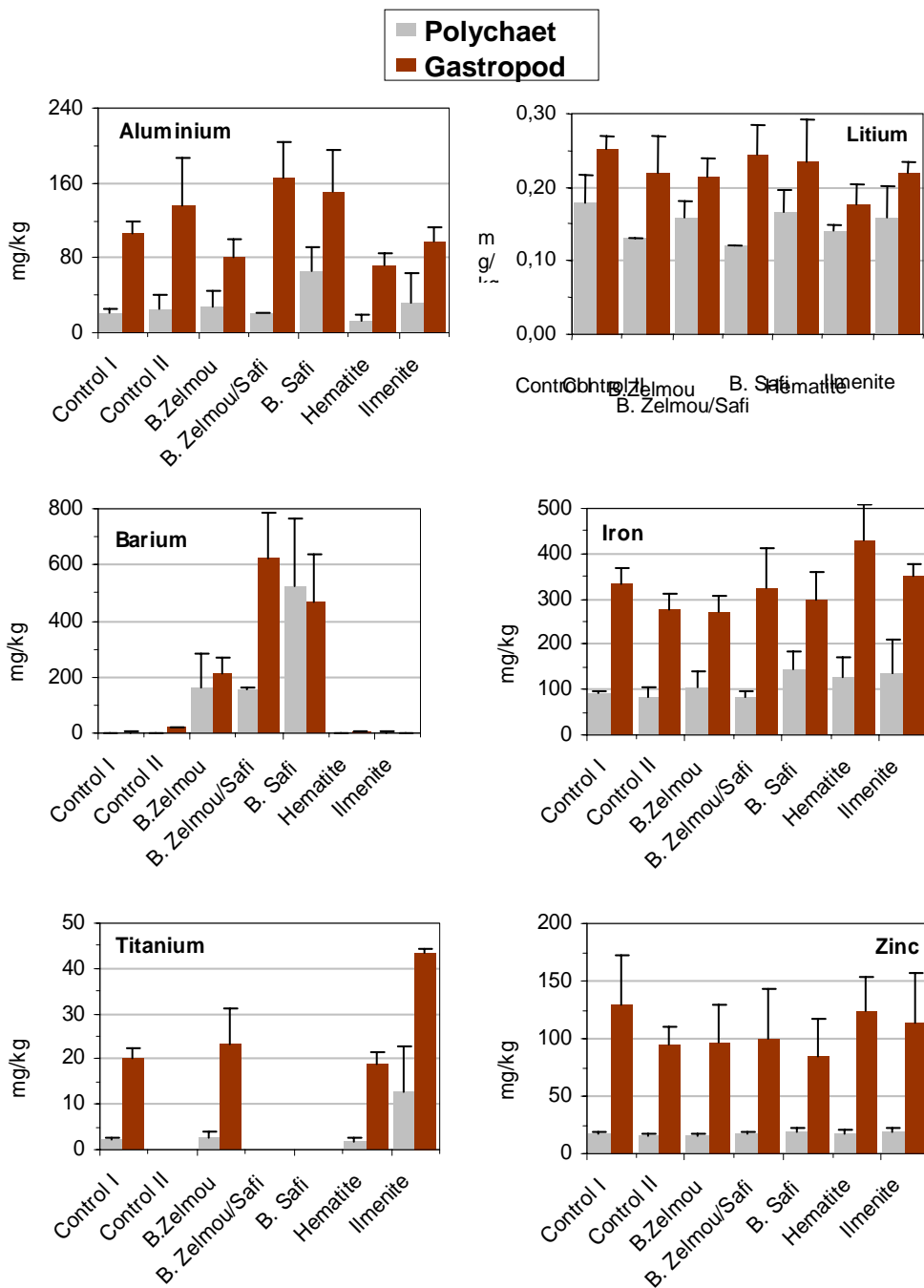


Figure 7. Concentration of metals (Al, Li, Ba, Fe, Ti and Zn) in organisms after 28 days exposure in control sediments or sediments spiked with test substances. Error bars = 1 standard deviation.