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Bioavailability of heavy
metals in drilling muds

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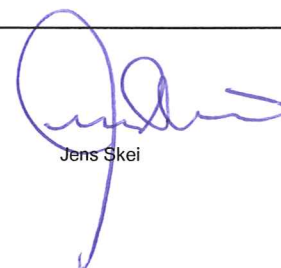
Abstract

Experimental work on uptake of metals from sediments spiked with barite, ilmenite and hematite were performed using the ragworm *Nereis diversicolor* and the netted dog whelk *Hinia (Nassarius) reticulata* as test organisms. The present 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 - an international research programme completed in December 2001. The review suggest low to moderate bioaccumulation and toxicity of metals in drill cuttings to marine organisms. The experimental work was performed in a standard test set-up at Solbergstrand Marine Research Station. The test determines enrichment ratios in exposed vs control organisms. Ratios of 67 and 76 for the respective species showed significant uptake of barium from marine sediments spiked with barite. Similarly, significant uptake of titanium were observed in organisms exposed to ilmenite. All other elements (Al, Li, Fe, Zn, Hg, Cd, Pb, Cu, Cr and Ni) showed no significant uptake and ratios within the range 0,6-1,5. This result was partly explained by anomalous low concentrations of Pb in the barite test substance, partly by the presence in several test substances of major fractions of Cr, Ni, Zn and Cu insoluble in standard nitric acid digestion (NS4770). Toxic effects of metals strongly bound in particulate mineral fractions are not expected.

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1. Tungmetaller	1. Heavy metals
2. Boreslam	2. Drilling mud
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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. The experimental work was performed in the soft-bottom mesocosm laboratories at Solbergstrand Marine Research Station in May-June 2002 by Anders Ruus and Sigurd Øksnevad. Co-authors Torgeir Bakke, Ketil Hylland and Frode Olsgard have contributed within their respective fields of expertise 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. Acknowledgements also to Oddbjørn Pettersen and Per Ivar Johannesen for technical assistance at Solbergstrand. Professional cooperation from Egil Mellgren and his colleagues at Norbar Minerals and M-I Norge has been beneficial to the project.

Oslo, 31.08.2002

Morten Thorne Schaanning

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Summary

The drilling of wells in offshore oil and gas exploration produce 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 components 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. One study has related inhibited enzyme activity in turbot to uptake of lead after exposure to barite with extremely high concentrations of lead. 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 uptake of metals from sediments spiked with barite and two alternative weight-materials for drilling muds, ilmenite (an oxide of iron and titanium) and hematite (an oxide of iron).

The three test-substances were analysed for total metals after digestion with hydrofluoric acid. Compared to Norwegian criteria for fjord and coastal sediments, concentrations in barite exceeded class I "high background" levels for copper (Cu) only and could be termed "moderately polluted". Hematite was "moderately polluted" with chromium (Cr). Ilmenite contained no detectable amounts of mercury (<0,005 mgHg/kg), but was "markedly polluted" with chromium and nickel, "moderately polluted" with copper and contained 3-10 times more zinc (Zn) than the two other test substances. Compared to information supplied from the contractor, the observed elemental composition appeared reasonably characteristic with regard to hematite and ilmenite, whereas the sample of barite contained less lead (Pb) than frequently reported. From the composition of the test substances used in the present study, substitution of barite with ilmenite in off-shore chemicals would reduce the total discharge of mercury and copper, but increase the discharges of chromium, zinc and nickel. Substitution with hematite would increase the discharge of chromium, but reduce the discharge of the other metals.

Two different species, the ragworm *Nereis diversicolor* and the netted dog-whelk *Hinia (Nassarius) reticulata* were exposed in seawater aquaria with a layer of spiked sediment. After four weeks, metal concentrations in sediment and purified biological samples were determined after standard nitric acid digestion (NS4770). Ratios between concentration in organisms living in spiked sediments and concentration in organisms living in non-spiked control sediments (enrichment ratios), were used as indications on uptake.

Enrichment ratios of 67 and 76 for the respective species showed significant uptake of barium from marine sediments spiked with barite. Similarly, enrichment ratios of 5,7 and 2,2 showed significant uptake of titanium from sediments spiked with ilmenite. No other metals showed significantly increased concentrations (ANOVA, Tukey HSD, $\alpha=0,05$) in organisms exposed to any of the test substances. Mercury from barite gave elevated concentrations in the spiked sediments (enrichment ratio = 4,4), but was apparently not taken up in the test organisms (enrichment ratios = 0,9 for both species). Chromium from ilmenite and hematite showed frequently up as slightly elevated enrichment ratios both in sediments and organisms, but concentrations in organisms exposed to the test substances were never more than 1,4x times higher than control organisms.

From a 4:1 mixing ratio calculated concentrations in spiked sediments were frequently higher than those observed. This applied to Zn, Cu, Cr and Ni in ilmenite, Cr in hematite and Cu in barite. This discrepancy most likely resulted from the different extraction techniques (hydrofluoric vs nitric acid), showing that the major fraction of these elements were present in the weight materials in phases insoluble in standard nitric acid digestion (NS4770). Particles may be taken up in organisms by phagocytosis, and the absence of observed uptake of these metals in the present study may have been due to inadequate extraction techniques. Nevertheless, being firmly bound in mineral particles these metal fractions as well as most of the barium in barite and titanium in ilmenite are not expected to produce toxic effects in marine organisms.

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).

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 uptake 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. 3.3.1, 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, barite, or ilmenite (Figure 1).

The experiment was conducted by the use of an established test system (Hylland, 1996) for the testing of bioavailability of environmental contaminants in marine sediments. The system installed in the soft-bottom mesocosm laboratories can be viewed in Figure 2. 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 Material and methods

3.2.1 Control sediment

Sediment for the experiment 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). Metal concentrations in this sediment are given in Table 1 ("Observed in control..."). The sediment had an organic carbon content of 5,3 µg/mg dry sediment and 73 % of the particles were smaller than 63 µm. The sediment was homogenised using a cement mixer (used only for sediments) before initiation of the experiment.

3.2.2 Test substances

The three test substances hematite, barite 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.

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).

Before initiation of the experiment, aliquots of the homogenised control sediment were spiked with hematite, barite or ilmenite (4:1 volume:weight ratio). 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 the homogenisation.

3.2.3 Organisms

Two species are used in the experimental set-up. One is the ragworm, *Nereis diversicolor* (Polychaeta) and the other is the netted dog whelk, *Hinia (Nassarius) reticulata* (Gastropoda). Both species are very common. 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. Besides species used in aquaculture, the ragworm is probably the most studied marine invertebrate. *Nereis* has also been used in bioaccumulation studies by others (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. Netted dog whelks and ragworms were collected on the same location as the control sediment. Before use, the organisms were acclimated for ≥ 1 week, in water from 60 m depth, at NIVA's marine research station at Solbergstrand.

3.2.4 Experimental set-up

The set-up (Figure 2) consisted 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 or ilmenite.

A detailed description of the experimental set-up can be found in NIVA-report 3537-96 (Hylland, 1996). The experiment was initiated on May 27th 2002 and terminated on June 24th 2002 (running a total of 28 days). An exposure time of 28 days was recommended by Lee et al. (1991). Subsamples for chemical analysis of the sediments were taken before transfer to the glass aquaria (15 × 20 × 22 cm). Approximately 1.5 L of sediment was added to each aquarium. Then the aquaria were fitted with separate flows of water supplied from 60 m depth in the Oslofjord nearby the Marine Research Station at Solbergstrand. Similar temperatures in all aquaria were obtained by the use of a water bath (also with water from 60 m depth). Finally the organisms were added to the tanks (20 polychaetes and 10 gastropods in each aquarium).

3.2.5 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 rests 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 °C before chemical analysis. Since each glass tank was an experimental unit (avoids pseudoreplication) all individuals of the same species from each tank were pooled into one sample.

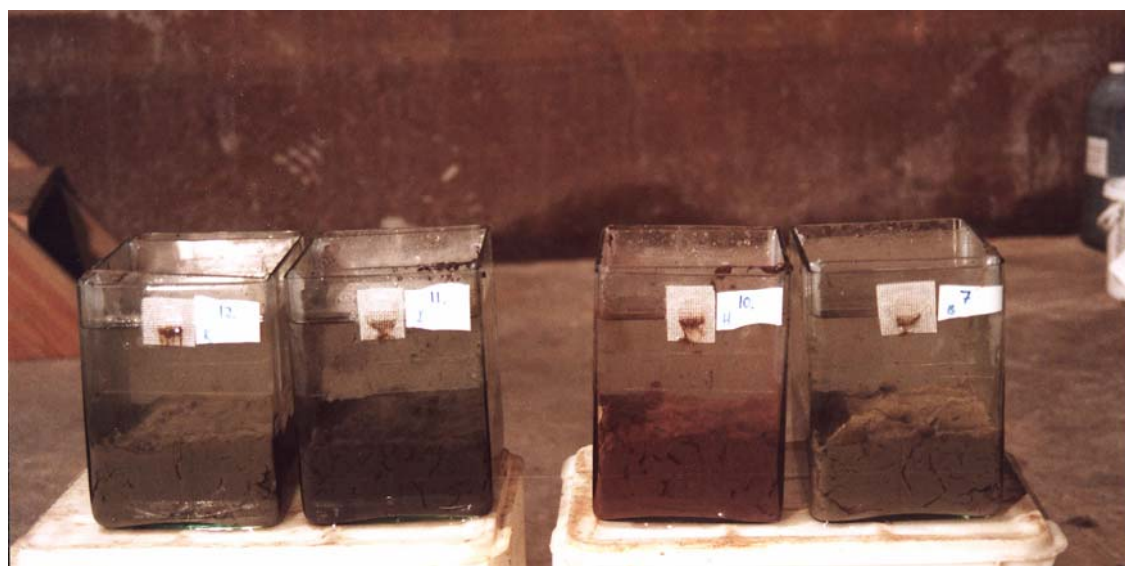


Figure 1. From left: Control (unspiked) sediment and sediment spiked with ilmenite, hematite and barite.

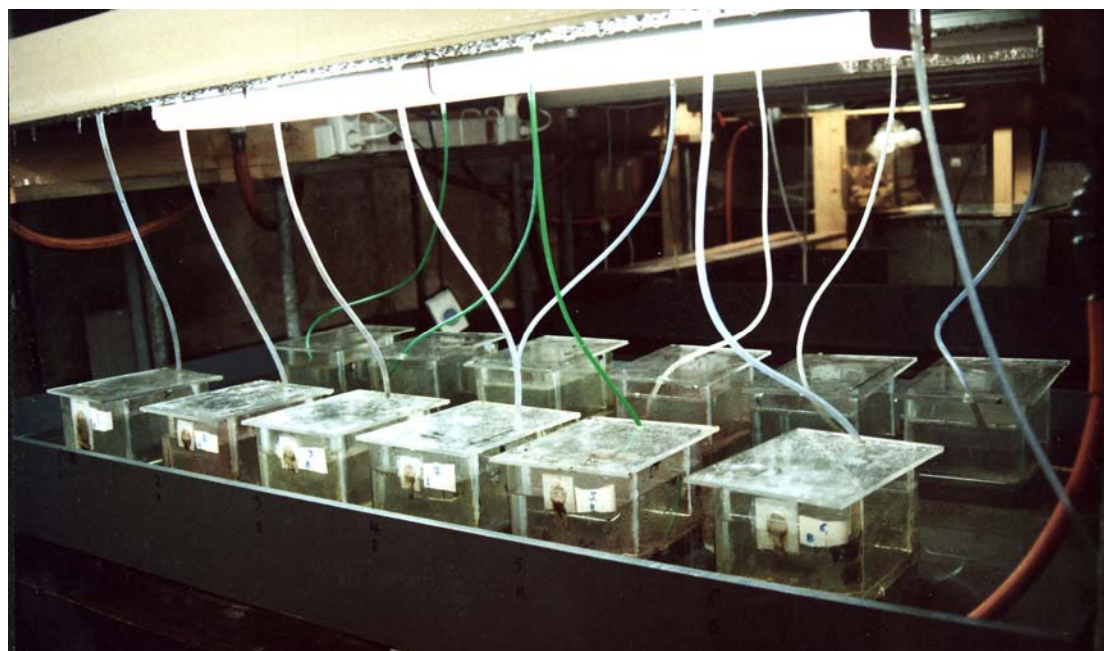


Figure 2. The experimental set-up involved a total of 12 glass aquaria (three replicates x four treatments).



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

Table 1. Observed concentrations (mg/kg) in test substances and spiked sediments compared with national criteria 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	<0,150	<0,250	<30	<35	<70	<30	20
Class II "Moderately polluted"										35-150	70-300	130-600	
Class III "Markedly polluted"											300-1500		
<i>Test substances (analysed with HF)</i>													
Barite	1370	2	24800	29	9700	35	0,130	0,060	10	74	19	3	2
Ilmenite	3570	2	345000	252000	1500	100	0,005	0,030	8	38	469	147	<2
Hematite	5660	2	221000	904	5970	10	0,009	0,030	10	11	156	10	<2
<i>Control and spiked sediments (analysed with HNO₃)</i>													
Barite	7200	11	12800	616	7320	34	0,083	0,060	8,4	17,2	16,6	12,0	-
Ilmenite	7590	11	14600	980	269	33	0,020	0,049	6,2	10,8	21,4	18,3	-
Hematite	7520	11	18000	632	890	33	0,018	0,046	6,7	9,0	33,3	13,9	-
Control	8620	13	14100	707	57	37	0,019	0,050	7,0	8,9	17,4	14,5	-
<i>Observed/predicted</i>													
Barite	100 %	102 %	79 %	108 %	369 %	94 %	201 %	115 %	111 %	78 %	94 %	98 %	-
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 %	-

3.2.6 Chemical analysis

The chemical analyses were performed at NIVA's laboratory. The three 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. BaSO₄).

Spiked sediments and biological samples were analysed after dissolution in HNO₃ 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.

3.3 Results

3.3.1 Test substances and spiked sediments

Element concentrations in test substances and spiked sediments are shown in Table 1 and Figure 4. Compared to annual weighted mean concentrations of ship-loads imported during the period 1994-2000 (Norbar Minerals, analytical reports 02.11.01), metal concentrations in the barite test substance were reasonably characteristic with regard to Zn, Cd, Cu, Cr and Ni, but the concentration of Pb (Table 1) was 7-62 times lower than the annual mean values of 70-623 mgPb/kg. The concentration of 0,13 mgHg/kg (Table 1) was higher than the annual means of 0,04-0,07 mg/kg in 1997-1998, but less than the annual means of 0,38-0,59 mg/kg in 1999-2000.

The composition of the ilmenite test substance (Table 1) 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). Analyses performed using NS4770 (West Lab Services AS, 03.08.01) showed much lower concentrations of Al (830 mg/kg), Fe (3400 mg/kg), Zn (5,0 mg/kg), Cu (3,2 mg/kg), Cr (1,9 mg/kg) and Ni (1,4 mg/kg), but similar concentrations of Hg, Cd and Pb. This difference might of course, result from occasional variations between samples from different ores even within the same geographical area (Leuterman et al. 1997), but is more likely to result from different extraction methods. Likewise, a sample of hematite analysed by West Lab Services AS in accordance with NS4770 (sample no. 2001-02726-1) showed lower concentrations of Al (1800 mg/kg), Fe (51000 mg/kg), and Cr (5,3 mg/kg) than those given in 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 not available for NS4770 extraction.

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 three 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

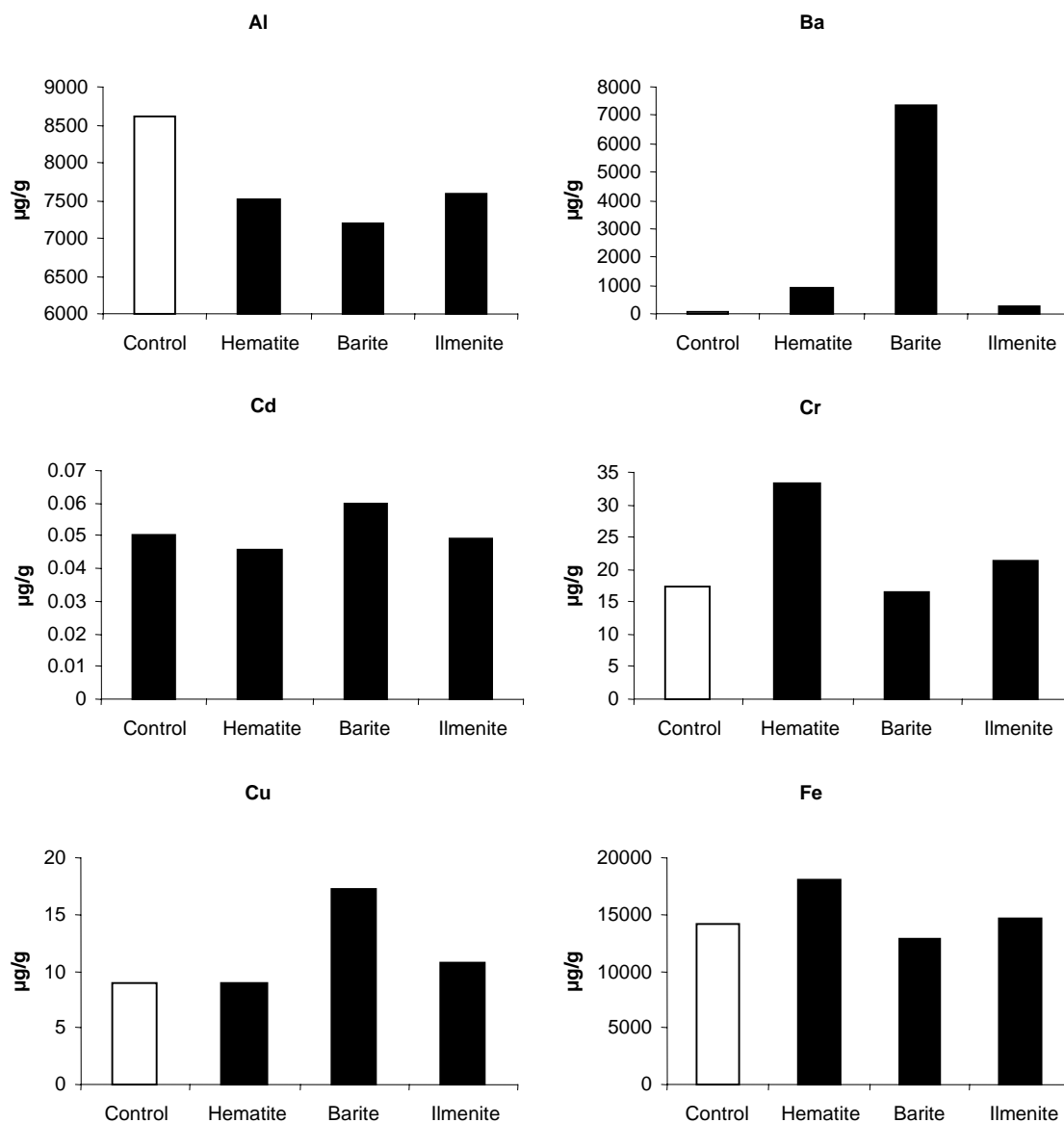


Figure 4. Metal concentrations in control sediments or sediments spiked with hematite, barite or ilmenite. (Al = aluminium, Ba = barium, Cd = cadmium, Cr = chrome, Cu = copper, Fe = iron). Continues next page....

presence of significant insoluble (in HNO_3) fractions of Fe, Ba and Cr in hematite and Fe, Ti, Ba, Zn, Cu, Cr and Ni in ilmenite and Fe and Cu in barite.³

The results from the HNO_3 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

³ Positive deviations for barium in barite and mercury in barite and ilmenite have no obvious explanations, but may result from sample inhomogeneities or analytical errors. Barium e.g. 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.

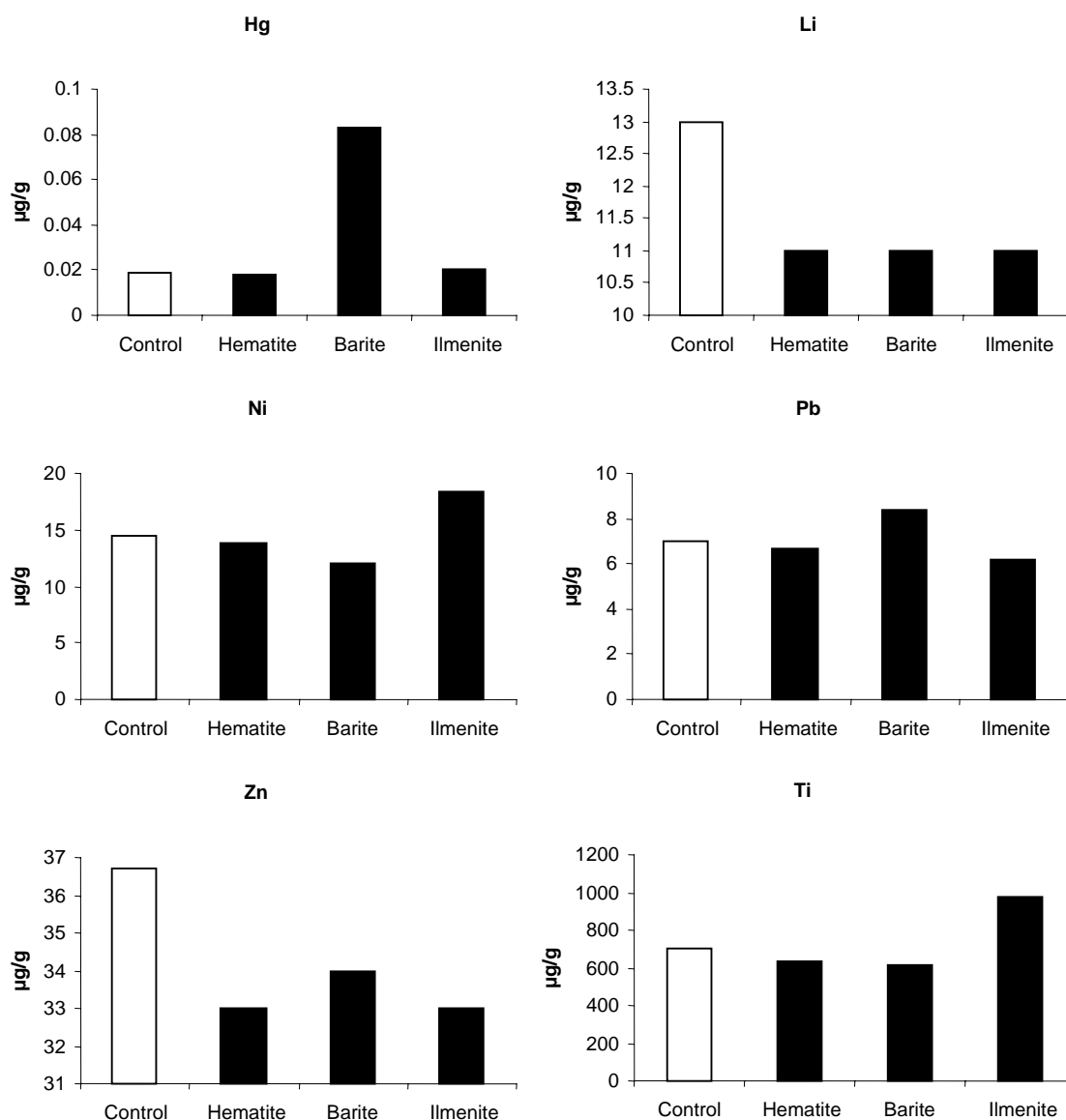


Figure 4. Continued.....Concentrations in sediment. Hg = mercury, Li = lithium, Ni = nickel, Pb = lead, Zn = zinc, Ti = titanium.

element in HNO_3 applied to all test substances and ilmenite in particular. Barite showed low yields of Fe and Cu only. Elements bound in mineral fractions may be taken up in animal tissues by phagocytosis, but not soluble in HNO_3 they are not likely to be mobilised in the organism and their physiological impacts (toxicity) should be small.

Compared to national environmental criteria for coastal and fjord sediments (Molvær et al. 1997), the data given in Table 1 shows that in all test substances the concentration of Zn, Hg, Cd, Pb and As were below the upper limits for class I “insignificantly polluted”. Barite was moderately polluted with copper, and hematite was moderately polluted with chromium. Ilmenite was moderately polluted with copper and markedly polluted with chromium and nickel. In the spiked sediments, however, none of the heavy metals exceeded the upper limit for class I.

Bioaccumulation

Metal concentrations in the organisms living on the different sediments are shown in Figure 5 (polychaetes) and Figure 6 (gastropods). As a quantitative measure of bioaccumulation, (enrichment) ratios between metal concentrations in animals living on spiked sediments and metal concentrations in animals living on control sediments were calculated and shown in Table 2. High enrichment ratios indicate bioaccumulation. For comparison, Table 2 also shows ratios between metal concentrations in spiked sediments and metal concentrations in the control sediment.

Ba

The results show that barium (Ba) in barite-spiked sediment was subject to bioaccumulation (Table 2, Figure 5, Figure 6). Significantly higher concentrations of Ba were observed in organisms exposed to barite-spiked sediments than in organisms exposed to control sediments (ANOVA, Tukey HSD, $\alpha=0.05$). Barite-spiked sediment contained ~130 times higher Ba-concentrations than the control sediment (Table 2, Figure 4), and polychaetes living on this sediment accumulated Ba-concentrations that were ~67 times higher than Ba-concentrations in polychaetes living on control sediment (Table 2, Figure 5). Due to the large variance in Ba-concentrations in polychaetes living on barite-spiked sediment, the non-parametric Mann-Whitney U test was performed to evaluate differences in Ba concentrations between barite exposed polychaetes and control polychaetes. The differences were significant.

Gastropods living on barite-spiked sediment confirmed a similar accumulation (~76 times) of barium (Table 2, Figure 6). The Ba concentrations in barite-exposed gastropods were significantly higher than in gastropods from any of the other sediments (ANOVA, Tukey HSD, $\alpha=0.05$).

Sediment concentrations of barium were higher than control, not only in barite-spiked sediments, but also in hematite-spiked (~16 times) and ilmenite-spiked (~5 times) sediments (Table 2). However, apart from a weak signal of 1,5 times (not significant) for gastropods on hematite-spiked sediments (Table 2), no evidence was found for bioaccumulation of barium from test-substances other than barite.

Ti

The results show that also titanium (Ti) in ilmenite-spiked sediment was subject to bioaccumulation (Table 2, Figure 5, Figure 6). Significantly higher concentrations of Ti were observed in organisms exposed to ilmenite-spiked sediments than in organisms exposed to control sediments (ANOVA, Tukey HSD, $\alpha=0.05$). Ilmenite-spiked sediment contained 1,4 times higher Ti-concentrations than the control sediment (Table 2, Figure 4), and polychaetes living on this sediment accumulated Ti-concentrations that were 5,7 times higher than Ti-concentrations in polychaetes living on control sediment (Table 2, Figure 5). Due to the large variance in Ti-concentrations in polychaetes living on ilmenite-spiked sediment, the non-parametric Mann-Whitney U test was performed to evaluate differences in Ti concentrations between ilmenite exposed polychaetes and control polychaetes. The differences were significant.

Gastropods living on ilmenite-spiked sediment confirmed a similar accumulation (2,2 times) of titanium (Table 2, Figure 6). The Ti concentrations in ilmenite-exposed gastropods were significantly higher than in gastropods from any of the other sediments (ANOVA, Tukey HSD, $\alpha=0.05$).

Table 2. Ratios between metal concentrations in sediments spiked with hematite, barite or ilmenite and concentrations in control sediment, and ratios between metal concentrations in organisms (polychaetes, *Nereis diversicolor* and gastropods, *Hinia (Nassarius) reticulata*) living on sediments spiked with hematite, barite or ilmenite and metal concentrations in organisms living on control sediment.

	SEDIMENT	POLYCHAETE	GASTROPOD
<u>Hematite:Control</u>			
Aluminum (Al)	0.9	0.6	0.7
Titanium (Ti)	0,9	0,8	0,9
Barium (Ba)	15.7	0.8	1.5
Cadmium (Cd)	0.9	0.9	0.9
Chromium (Cr)	1.9	1.0	1.4
Copper (Cu)	1.0	0.9	1.2
Iron (Fe)	1.3	1.4	1.3
Nickel (Ni)	1,0	1,0	0,7
Lead (Pb)	1,0	0,8	0,7
Zinc (Zn)	0,9	1,1	1,0
Mercury (Hg)	0.9	0.8	1.2
Litium (Li)	0.8	0.8	0.7
<u>Barite:Control</u>			
Aluminum (Al)	0.8	1.3	0.7
Titanium (Ti)	0,9	1,2	1,2
Barium (Ba)	129.3	66.7	75.5
Cadmium (Cd)	1.2	0.9	0.7
Chromium (Cr)	1.0	1.0	0.9
Copper (Cu)	1.9	1.2	0.7
Iron (Fe)	0.9	1.1	0.8
Nickel (Ni)	0,8	1,1	0,8
Lead (Pb)	1,2	1,1	0,9
Zinc (Zn)	0,9	0,9	0,8
Mercury (Hg)	4.4	0.9	0.9
Litium (Li)	0.8	0.9	0.8
<u>Ilmenite:Control</u>			
Aluminum (Al)	0.9	1.5	0.9
Titanium (Ti)	1,4	5,7	2,2
Barium (Ba)	4.8	0.9	0.8
Cadmium (Cd)	1.0	1.0	0.6
Chromium (Cr)	1.2	1.3	1.4
Copper (Cu)	1.2	1.0	1.2
Iron (Fe)	1.0	1.5	1.1
Nickel (Ni)	1,3	1,3	0,7
Lead (Pb)	0,9	1,2	0,8
Zinc (Zn)	0,9	1,1	0,9
Mercury (Hg)	1.1	0.9	0.9
Litium (Li)	0.8	0.9	0.9

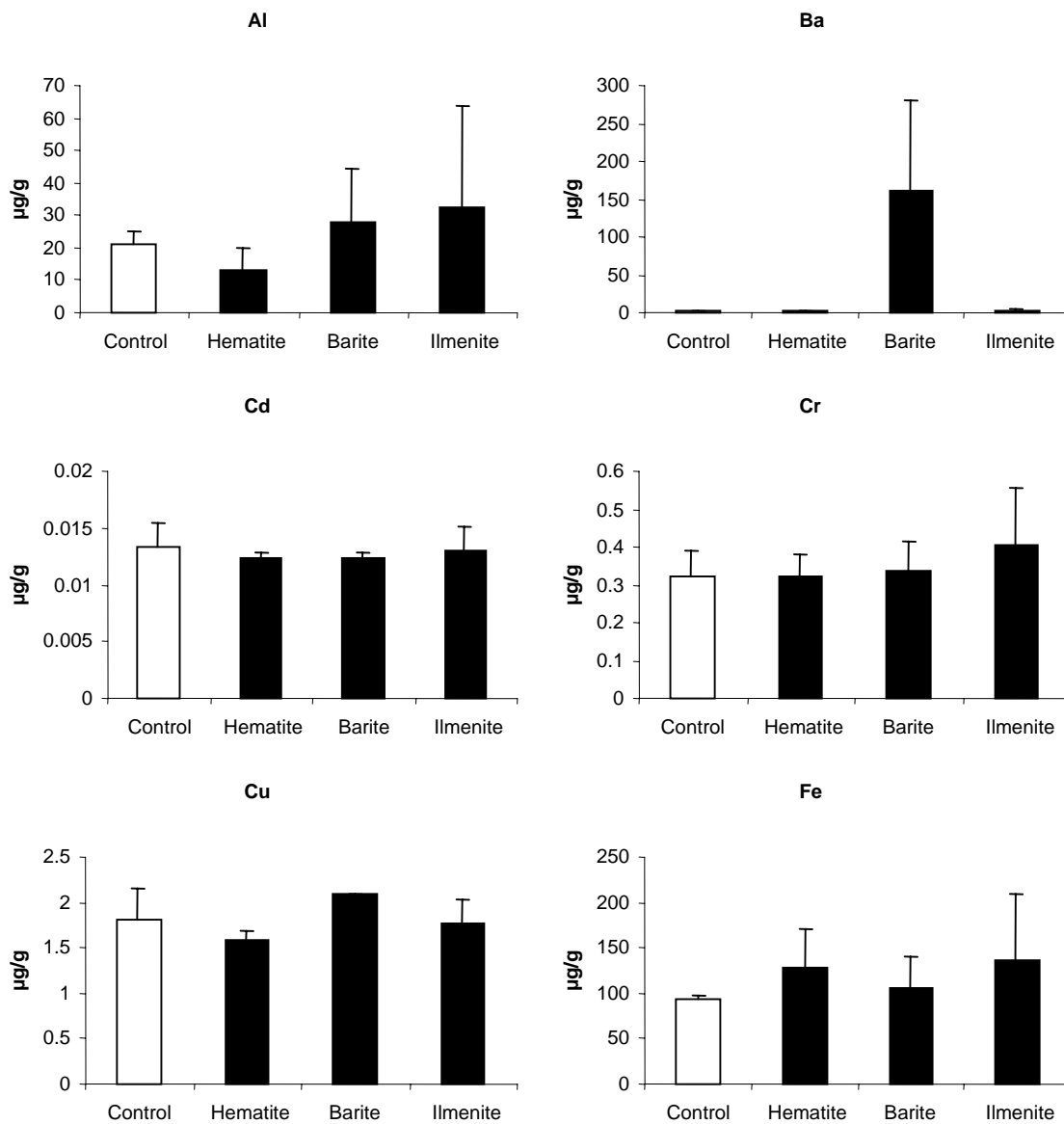


Figure 5. Metal concentrations in ragworm, *Nereis diversicolor* (Polychaeta) living on control sediments or sediments spiked with hematite, barite or ilmenite. The concentrations are mean of three replicate samples (aquaria). Error bars = one standard deviation. Al = aluminium, Ba = barium, Cd = cadmium, Cr = chrome, Cu = copper, Fe = iron, Hg = mercury, Li = lithium.

Hg

The concentrations of mercury (Hg) was 4,4 times higher in barite-spiked sediments than in the control sediment (Table 2), but ratios of 0,9 for both species gave no evidence for bioaccumulation of Hg from barite.

Cr

In spite of the relatively high concentration of Cr in the ilmenite test substance, highest concentration of this metal showed up in the hematite spiked sediments (Table 1) with an enrichment factor of 1,9

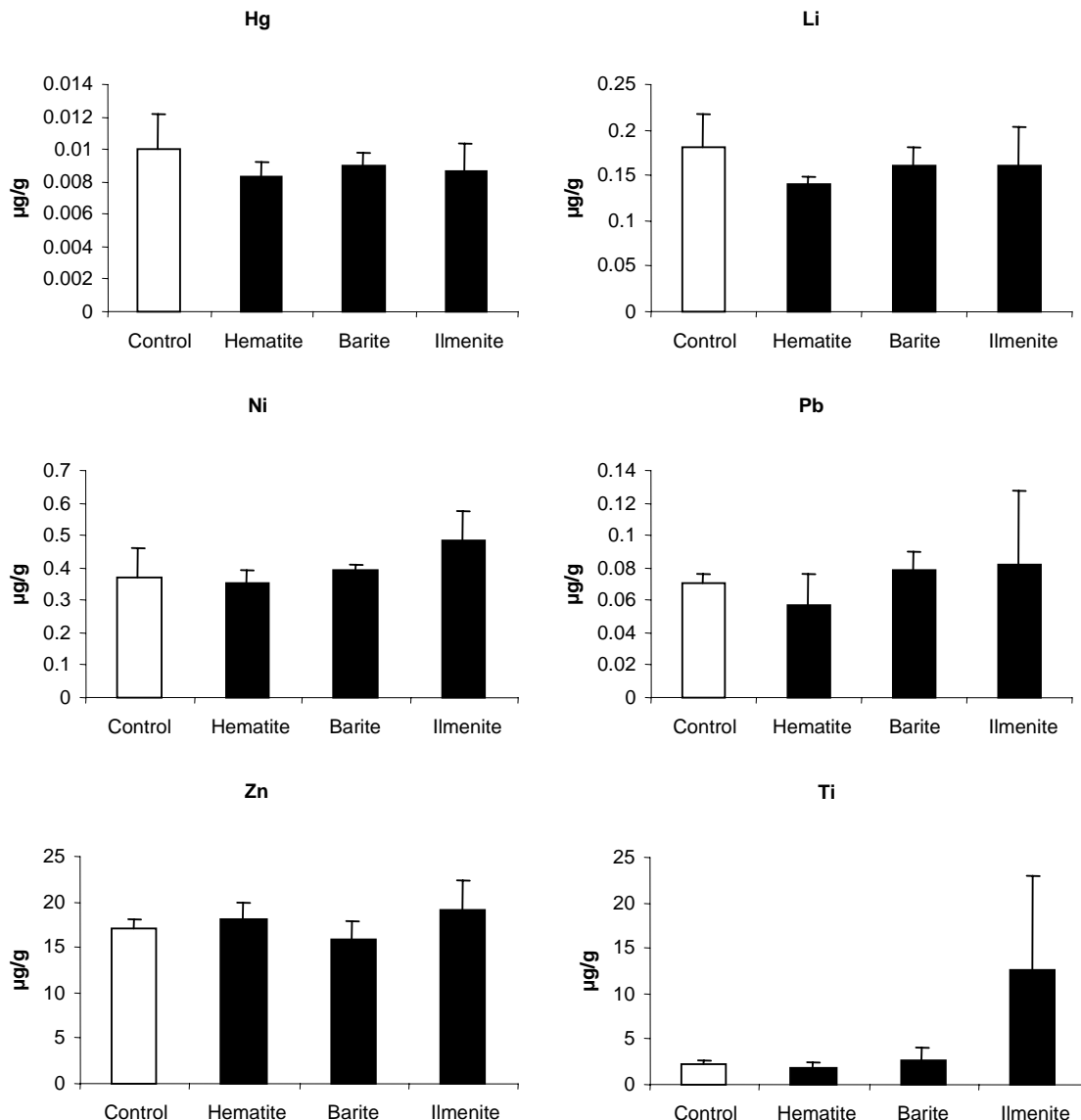


Fig. 5. Continued...Concentrations in ragworm. Hg = mercury, Li = lithium, Ni = nickel, Pb = lead, Zn = zinc, Ti = titanium.

relative to control sediments (Table 2). The concentration of Cr in polychaetes from the hematite spiked sediments were, however, identical (ratio = 1,0) to those from control sediments, whereas the gastropods were slightly higher with a ratio of 1,4 (not significant).

Ni

Also the concentration of Ni was relatively high in the ilmenite test substance (147 mg/kg as compared to 3 mg/kg in barite and 10 mg/kg in hematite). This difference yielded only a small enrichment of test

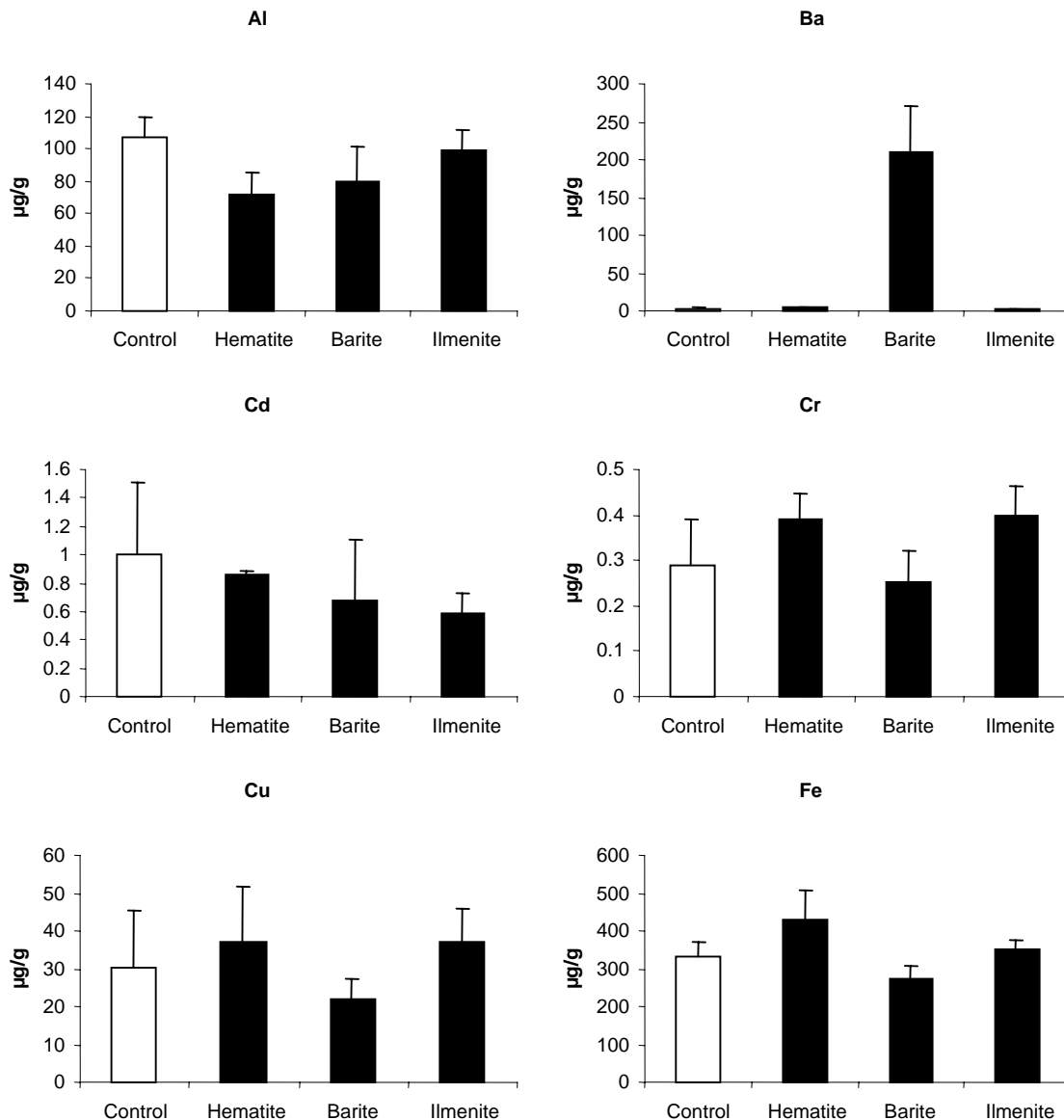


Figure 6. Metal concentrations in netted dog whelk, *Hinia (Nassarius) reticulata* (Gastropoda) living on control sediments or sediments spiked with hematite, barite or ilmenite. The concentrations are mean of three replicate samples (aquaria). Error bars = one standard deviation. Al = aluminium, Ba = barium, Cd = cadmium, Cr = chrome, Cu = copper, Fe = iron.

sediment and polychaetes (both ratios = 1,3) (not significant) (Table 2), whereas the gastropods in the ilmenite treatment contained less Ni than the gastropods in the control sediments (ratio = 0,7).

Cu

In test substances and spiked sediments the concentrations of Cu ranked barite>ilmenite>hematite. Enrichment ratios vs control sediments were up to 1,9 in the barite treatment. In the organisms, however, the ratios appeared to vary at random between 0,7 and 1,2 (Table 2).

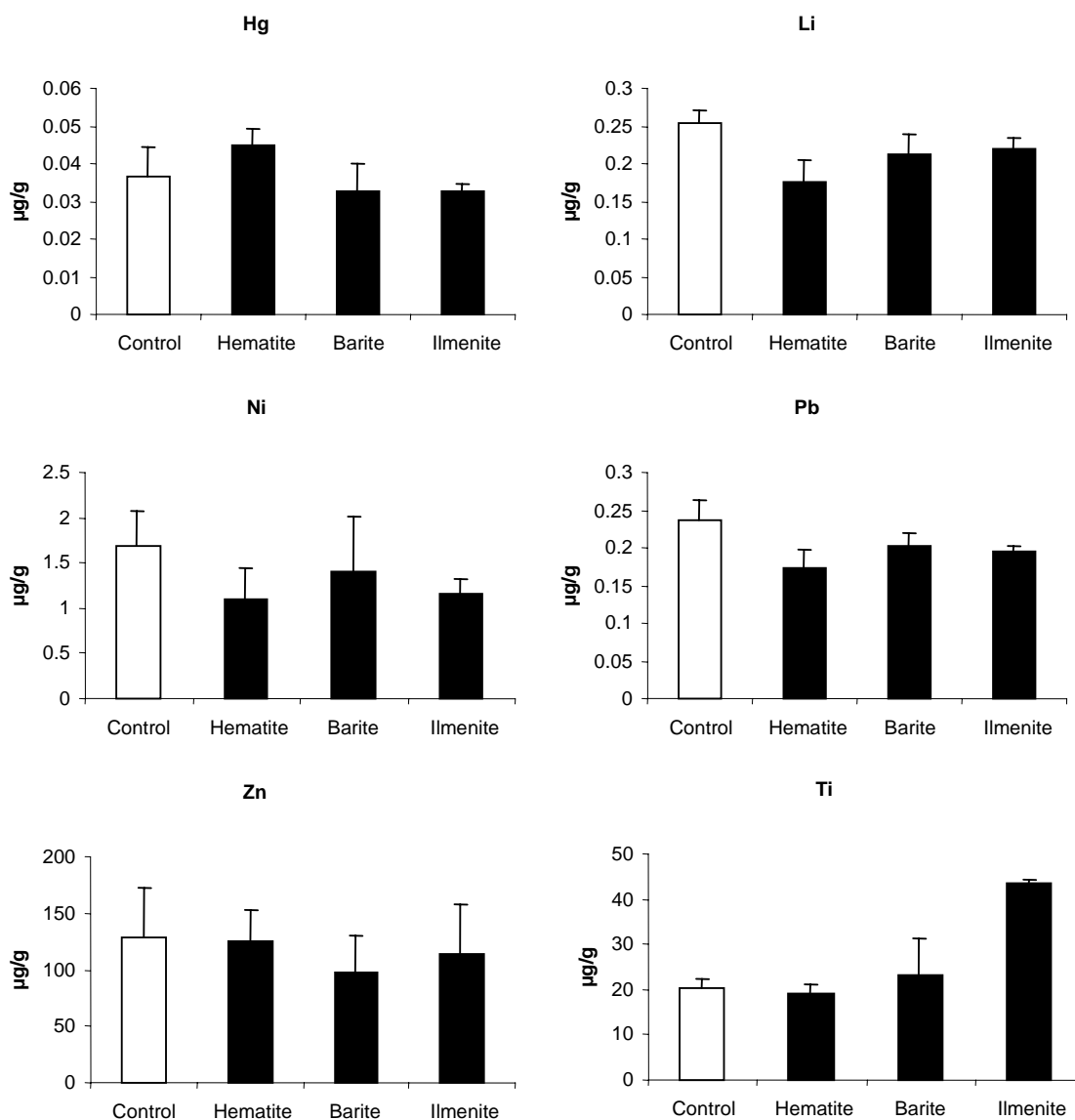


Figure 6 Continued.....Concentrations in dog whelk. Hg = mercury, Li = lithium, Ni = nickel, Pb = lead, Zn = zinc, Ti = titanium.

3.4 Conclusions from experimental work

The three test substances appeared representative with regard to previously reported concentrations of Ba, Ti, Fe, Al, Zn, Hg, Cd, Cu, Cr and Ni. Also Pb in ilmenite and hematite was reasonably representative. The concentration of Pb in barite may vary widely as a result of minerals taken from different ores/mines. Unfortunately, the present test substance (10 mgPb/kg) was within the lower range of Pb-concentrations reported for barite and low also compared to annual weighted average of 70-263 mg/kg for ship-loads of barite imported during the period 1994-2000.

Being not different from the control sediment, does not mean that highly bioavailable phases of Pb in the barite might not show up as enrichments in the test organisms, but when the concentration in the sediment is as low as in the present test, bioaccumulation cannot be easily detected. Therefore the test is inconclusive with regard to the potential bioavailability of the lead frequently present in barite.

The barite-spiked test sediment was clearly enriched with Hg (4,4x). However, organisms exposed to this sediment were not enriched (0,9x in both organisms). It was possible, therefore, to conclude that the Hg present in this barite was not bioavailable. Similarly, indications were found that the Ba present in ilmenite and hematite was not bioavailable. Chromium was enriched in the hematite-spiked sediment (1,9x). The polychaetes showed no enrichment (1,0x) but the 1,4x enrichment in the gastropods showed some uptake in this organism. Chromium enrichments of 1,2x-1,4x in sediment and organisms indicated some uptake of chromium in the ilmenite treatment as well.

Significant uptake was only observed with regard to Ba from barite-spiked sediments and Ti from ilmenite spiked sediments.

Refractory phases of Cu in barite, Cr in hematite and Cu, Cr and Ni in ilmenite yielded concentrations in test substances beyond the upper limit for class I “insignificantly polluted”. These phases were, however, not detectable using NS4770 extraction and hence not likely to produce adverse effects in marine organisms.

4. Conclusion

The experimental work and the literature surveyed appears reasonably consistent with regard to biological uptake of Ba. Uptake of metals such as Hg, Pb and Cd have been shown in other studies or is likely to occur from sediments more heavily contaminated than the sediments used in this study, but if present, 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 as 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 extremely high concentrations of lead. 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.

From the composition of the test substances used in the present study, replacement of barite with ilmenite would reduce the total discharge of mercury and copper, but increase the discharges of chromium, zinc and nickel. Replacement with hematite would increase the discharge of chromium, but reduce the discharge of the other metals. Being mainly present in fractions insoluble in nitric acid, adverse effects on marine organisms from the heavy metals associated with ilmenite or hematite are not expected.

The experimental work showed significant uptake of barium from sediments spiked with barite and significant uptake of titanium from sediments spiked with ilmenite. No other metals showed significantly increased concentrations in organisms exposed to any of the test substances. The mercury associated with barite produced elevated concentrations in the spiked sediments (enrichment ratio = 1,4), but was apparently not taken up in the test organisms (enrichment ratios = 0,9 for both species). Chromium produced frequently elevated enrichment ratios (1,0-1,4) in test organisms exposed to sediments spiked with ilmenite and hematite.

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