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Estimation of Bioavailability of Metals from Drilling Mud Barite

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EDITOR'S NOTE:

This is 1 of 5 papers reporting on the results of a 4-year project to develop an environmental risk-based decision support tool, to assist the oil industry in establishing cost-effective measures for reducing risk to the marine environment from drilling discharges.

ABSTRACT

Drilling mud and associated drill cuttings are the largest volume wastes associated with drilling of oil and gas wells and often are discharged to the ocean from offshore drilling platforms. Barite ($BaSO_4$) often is added as a weighting agent to drilling muds to counteract pressure in the geologic formations being drilled, preventing a blowout. Some commercial drilling mud barites contain elevated (compared to marine sediments) concentrations of several metals. The metals, if bioavailable, may harm the local marine ecosystem. The bioavailable fraction of metals is the fraction that dissolves from the nearly insoluble, solid barite into seawater or sediment porewater. Barite–seawater and barite–porewater distribution coefficients (Kd) were calculated for determining the predicted environmental concentration (PEC; the bioavailable fraction) of metals from drilling mud barite in the water column and sediments, respectively. Values for $Kd_{barite–seawater}$ and $Kd_{barite–porewater}$ were calculated for barium, cadmium, chromium, copper, mercury, lead, and zinc in different grades of barite. Log $Kd_{barite–seawater}$ values were higher (solubility was lower) for metals in the produced water plume than log $Kd_{barite–porewater}$ values for metals in sediments. The most soluble metals were cadmium and zinc and the least soluble were mercury and copper. Log K_d values can be used with data on concentrations of metals in barite and of barite in the drilling mud–cuttings plume and in bottom sediments to calculate $PEC_{seawater}$ and $PEC_{sediment}$.

Keywords: ERMS Drilling discharges Barite Heavy metals

INTRODUCTION

Drilling muds and drill cuttings are the wastes produced in largest volumes during drilling onshore and offshore oil and gas wells. Drilling muds are specially formulated mixtures of natural or modified clays and/or polymers, weighting agents, and smaller amounts of other solid and liquid chemicals suspended in water (i.e., water-based drilling muds [WBM]), a refined petroleum product (i.e., oil-based drilling muds [OBM]), or a synthetic organic liquid (i.e., synthetic-based drilling muds [SBM]; OGP 2003; Melton et al. 2004; Neff 2005). The most important functions of drilling muds are to transport drill cuttings to the surface; balance subsurface and formation pressures, preventing a blowout; and cool and support part of the weight of the drill pipe and bit.

Drill cuttings are particles of crushed formation rock generated by the grinding action of the drill bit. During drilling, the drilling mud is pumped continuously down the hollow core of the drill pipe; it exits through the drill bit and sweeps cuttings up the annulus (i.e., the space between the drill pipe and the wall of the well) to the surface. Drill cuttings are separated from the drilling mud on the drilling rig; the drilling mud is then recirculated down-hole. During drilling from offshore platforms, drill cuttings usually are treated to remove most of the drilling mud solids and then discharged to the ocean, if permitted by local environmental regulations.

Regulation of ocean discharge of drilling muds and cuttings

Most drilling of offshore oil and gas wells in the North Sea, the US Gulf of Mexico, and other offshore production areas throughout the world is performed with WBM (Neff et al. 2000; OGP 2003; Melton et al. 2004; Neff 2005). This is due to strict regulations on ocean discharge of OBM and SBM and associated cuttings. Discharge of cuttings contaminated with diesel-based OBM was prohibited in 1984 to offshore waters of European countries that are signatories to the Oslo–Paris Convention for the Protection of the Marine Environment of the North-East Atlantic (OSPAR); OSPAR prohibited discharge of cuttings containing any type of OBM in 1996 (OSPAR 1999). Synthetic-based drilling muds were designed as less environmentally harmful drilling muds than OBM. Although they were first used in the North Sea, they have been used rarely there since 2001, because of OSPAR (2000; Decision 2000/3), which states, "the discharge into the sea of cuttings contaminated with synthetic fluids shall only be authorized in exceptional circumstances." Cuttings produced during drilling with WBM are permitted for ocean discharge in the OSPAR countries and in Federal waters (i.e., >4.8 km from shore) of the US Gulf of Mexico (USEPA 1996). Synthetic-based drilling muds cuttings, but not OBM cuttings, also are permitted for discharge to offshore waters of the US Gulf of Mexico. Water-based drilling muds, but not OBM or SBM, may be permitted for ocean discharge to European and US offshore waters. Drilling waste discharge regulations vary widely in other offshore oil development areas in the world.

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Drilling waste discharges to the ocean are tightly regulated in most of the world because of concern about the physical impacts of solids and the toxicity of drilling waste chemicals in the water column and particularly in sediment ecosystems (US National Research Council 1983). Petroleum hydrocarbons and metals are the chemicals of greatest toxicological concern in drilling muds and cuttings. Drilling mud metals could cause environmental harm if they are present in the water column or sediments in soluble, bioavailable forms.

Oil companies operating in Norway sponsored the Environmental Risk Management System (ERMS) Project to develop environmental risk-based management tools to aid in achieving the goal of "zero harmful discharge" from offshore oil and gas operations in the Norwegian Sector of the North Sea. The ERMS Project developed methods to calculate an environmental impact factor (EIF) for ocean discharge of produced water from production platforms (Johnsen et al. 2000), and for ocean discharges of drilling wastes from offshore platforms (Smit et al. 2008; Singsaas et al. 2008). The risk assessment is performed as recommended by the European Union Technical Guidance Document (EC 2003). Environmental hazards of chemicals of concern in the drilling discharge are estimated as the ratio of the predicted environmental concentration (PEC) to the predicted no effect concentration (PNEC). The objective of this paper is to describe an approach for predicting the PEC of metals from drilling mud barite in the water column and sediments. These PECs are used to estimate the contribution of metals to the toxicity of drilling wastes in the water column and sediments (Altin et al. 2008), and to model the EIF for drilling discharges in the water column and sediments around offshore platforms (Rye et al. 2008).

Drilling mud barite

The 2 most abundant solids in most drilling muds are barite (i.e., barium sulfate [$BaSO_4$]) and bentonite clay. Bentonite is used to increase the viscosity of the drilling mud and, in many modern WBMs, is replaced by a water-soluble organic polymer, such as carboxymethylcellulose (Neff 2005). Barite is used as a weighting agent to counteract reservoir pressures. Because reservoir pressure usually increases with well depth, the concentration of barite in the drilling mud is increased as the well is drilled deeper (Neff et al. 1987).

Barite is a soft, dense (4.1–4.5 g/cm^3) natural mineral. Drilling mud barite is at least 92% pure (USEPA 1985), has a specific gravity greater than 4.2 g/cm^3, and 97 weight % must pass through a 75-µm screen, with no more than 30% smaller than 6 µm in diameter (API 1993). The median grain-size of drilling mud barite usually is maintained at 10 to 20 µm, so that it will remain in suspension during circulation through the drill string. Mineral impurities in barite include silica, iron oxide, limestone, and dolomite, as well as several metals, mostly in the form of mineralized metal sulfides.

Barite has a low aqueous solubility in seawater (81 µg barite/L or 48 µg barium/L) at 20 °C (Burton et al. 1968). The concentration of dissolved barium in seawater is controlled by equilibrium with solid barite. The solubility product (K_{sp}) of $BaSO_4$ at atmospheric pressure and 25 °C is approximately 1.05×10^{-10} M (Neff and Sauer 1995). At the high natural sulfate concentration of oxygenated seawater (~0.28 mM), particulate barite is quite stable in the water column and oxidized layers of sediment. Most ocean waters are undersaturated with respect to barite (Monnin et al. 1999; Rushdi et al. 2000; Monnin and Cividini 2006). Concentrations of barium in offshore waters of the oceans range from about 3 to about 34 µg/L (30–170 nM/kg) with concentrations usually increasing with depth (Neff 2002a).

Metals in drilling mud barite

Most of the metals sometimes detected in drilling muds are present primarily as trace impurities in barite, bentonite clay, or the sedimentary rocks (drill cuttings) in the formations penetrated by the drill bit. The metals of environmental concern (because of their toxicity) that may be present in some drilling mud barites at concentrations more than 10 times higher than their concentrations in clean marine sediments include cadmium, chromium, copper, mercury, lead, and zinc (Table 1). These metals are present in barite primarily as insoluble mineralized sulfide salts (Kramer et al. 1980; Trefry et al. 1986; Leuterman et al. 1997; Trefry and Smith 2003). These solid metal sulfides have limited environmental mobility and low toxicity to plants and animals (Neff 2002a, 2002b). Most barites also contain high concentrations of aluminum, iron, and silicon, associated primarily with mineral impurities in the barites. These metals also are abundant in clays and are not considered toxic to marine organisms. As shown in Table 1, barite containing low, essentially background concentrations of metals is commercially available for drilling mud formulation.

Behavior of metals associated with cuttings

When discharged at sea, WBM and WBM cuttings disperse over a wide area and settle to the sea floor (Neff et al. 1987). Synthetic-based drilling mud cuttings (SBM itself is not permitted for discharge) tend to clump and settle rapidly to the bottom near the discharge as large aggregates (Neff et al. 2000). Some of the unflocculated clay and barite particles in a WBM or WBM cuttings plume disperse in the water column over a wide area down-current from the discharge. The slow settling of these fine particles results in a short-term increase in concentrations of drilling waste chemicals dispersed or dissolved in the water column.

Accumulation of cuttings on the sea floor often results in an increase in the concentration of barium and sometimes several other metals in sediments near the discharge (Neff et al. 2000; Neff 2005). Barium concentration (i.e., from drilling mud barite) often exceeds 10000 µg/g in sediments on the sea floor near offshore drilling discharges (Ray and Neff 2003).

The metals in solid barite particles in the drilling mud plume in the water column and in the cuttings pile on the sea floor are not bioavailable. The bioavailable, and hence biologically active forms of metals with potential to harm marine organisms, are restricted to the chemical species that can cross the membranes of the organism and enter the interior of the cells (Neff 2002a). According to Simkiss and Taylor (1989), the permeable, bioavailable forms of metals are

- Free metal ions (e.g., M^{2+}),
- Hydrated ions (e.g., $M(H_2O)_6{}^{2+}$),
- Charged metal complexes (e.g., $MCl(H_2O)_5{}^{+}$),
- Uncharged inorganic complexes (e.g., $MCl_2{}^{0}$), and
- Some organometallic complexes (e.g., CH_3M^{n+})

The metals in solution in sediment porewater or in the drilling mud plume are more bioavailable and toxic than the solid metals (Simpson and Batley 2007). Thus, metals in drilling mud barite particles must dissolve from the particles

Table 1. Mean concentrations of metals in 4 samples of drilling mud barite used in metal solubility studies by Crecelius et al. (2007). MI-Low and NORBAR are typical of barite used today in drilling muds in the US Gulf of Mexico and Norway, respectively. MI-High and Lab Blend barites are similar to some used before 1993 in the US Gulf of Mexico. Metal concentrations in uncontaminated marine sediments are from Neff et al. (1987). Concentrations are μg/g dry wt (ppm)

Metal	MI-low	MI-high	Lab blend	NORBAR	Marine sediments
Barium	538000	524000	507000	NA	1–2000
Cadmium	0.35	0.77	7.0	0.05	0.1–0.6
Chromium	15	6.5	11	40	36–110
Copper	98	88	189	86	7–33
Iron	6600	9270	29600	25300	20000–60000
Mercury	0.44	5.9	6.7	0.05	0.03–0.14
Lead	318	243	1370	18	10–33
Zinc	35	167	2030	1211	27–88

MI-low = low trace metal barite; MI-high = a high trace metal barite; Lab blend = a laboratory blend of barites from several sources; NORBAR = Norwegian drilling mud barite.

into the ambient water in the drilling discharge plume or the porewater in the cuttings pile to become bioavailable and potentially toxic (if concentrations of bioavailable forms are high enough).

ESTIMATION OF PEC FOR METALS FROM BARITE IN THE WATER COLUMN

Most of the metals in drilling mud/cuttings, are in drilling mud barite. Although barite itself has a low solubility in seawater, most of the metals in drilling mud barite are present in even less soluble phases. They are associated with mineralized sulfide inclusions in the solid barite, particularly sphalerite (zinc sulfide) and pyrite (iron sulfide; Crecelius et al. 2007).

Mobilization of metals from barite into more biologically accessible forms (e.g., dissolved ions or ion complexes) is dependent on dissolution of solid metal sulfide inclusions in the nearly insoluble barite. Dissolution of metals is controlled in part by accessibility of the metals to the water phase at the solid–water interface (metals in the interior of insoluble particles have a low accessibility) and by the solubility product (K_{sp}) of the metal in association with the counter-ions (usually anions) in the ambient water. The K_{sp} is the product of the molar activities of the cation and anion in solution in equilibrium with the solid metal salt.

Because most of the metals in barite appear to be associated with sulfides, the solubility products of the metal sulfides are better indicators of the bioavailability of the different metals than the solubility of barite. Dissolution is controlled by the K_{sp} values for the different metal sulfides and the concentrations of labile sulfides in the ambient water. Seawater and porewater in oxidized layers of sediment contain a high concentration of inorganic sulfate that can be reduced to sulfide under reducing conditions (low Eh). Thus, metal dissolution from barite should be dependent on the oxidation–reduction potential (redox potential) of the water in contact with the solid barite. Sulfide may be produced in a hypoxic water column or it may diffuse into the water from suboxic sediments. Sulfide concentration may be high in the benthic boundary layer just above suboxic sediments (such as those in an organically enriched cuttings pile): Concentration decreases sharply with distance above the bottom (Johnson and Coletti 2002). Sulfide in sediment porewater and water in the benthic boundary layer may stabilize the metal sulfides in drilling mud barite.

Sulfide concentrations in oxic surface waters of the North Atlantic and the Mediterranean Sea are in the range of 0.9 to 2 nM and tend to increase with depth in the water column (Luther and Tsamakis 1989); concentrations are high enough to slow metal sulfide dissolution. The dissolved sulfide is present as metal sulfide clusters that are stable in oxic seawater (Luther and Rickard 2005).

The solid metals in barite can be released from the solid phase by dissolution into the ambient water, which is an equilibration process between the solid metal salt and the cationic and anionic species of the salt in solution, but not by simple adsorption–desorption partitioning. Only a few percent of the total of the metals of concern in drilling muds are in readily exchangeable forms, probably associated mainly with clay particles in the drilling mud (Deuel and Holliday 1998), and can be modeled by equilibrium partitioning theory (Hassan et al. 1996).

The dissolution of each metal of interest from solid barite into seawater is controlled by the solubility of its most stable, least soluble salt, which, for all the metals of interest, except barium and chromium, is the sulfide. Chromium does not form stable sulfides. The most stable form of chromium in marine sediments appears to be chromic hydroxide ($Cr(OH)_3$). The solubility products (log K_{sp}) of the most stable forms of the metals of interest in seawater and sediments are summarized in Table 2. Solubility products for nearly insoluble metal salts are difficult to estimate accurately, so published values for a particular metal may vary by up to about 1 order of magnitude. Therefore, estimates of dissolved metals concentrations in seawater and sediment porewater, based on solubility product may vary by this amount.

The solubility product is difficult to use to estimate concentrations of dissolved (bioavailable) metals in seawater and sediment porewater because the concentration of the metal in solution is dependent primarily on the concentration of the counter ion in solution, rather than the concentration of the metal in the solid phase. The concentration of sulfide usually is low in oxic surface waters but may be much higher in the benthic boundary layer just above the bottom (Johnson and Coletti 2002). Even in the absence of reactive sulfides, metal sulfides dissolve slowly in seawater (Luther and Rickard 2005).

Table 2. Solubility products (K_{sp}) of the dominant forms of metals in drilling mud barite. Data from Krauskopf and Bird (1995). K_{sp} is the product of the molar activities of the ions of a chemical compound in an aqueous solution in equilibrium with the solid chemical compound

Metal compound	K_{sp}	Metal compound	K_{sp}
$BaSO_4$	1×10^{-10}	HgS	5×10^{-54}
CdS	1×10^{-27}	NiS	2×10^{-27}
$Cr(OH)_3$	4×10^{-38}	PbS	3×10^{-28}
CuS	8×10^{-37}	ZnS	2×10^{-25}

Because of the slow kinetics (reaction rate) of dissolution of most metal sulfides, even at the low nanomolar sulfide concentrations in surface waters of the ocean, it is unlikely that metals in solution will reach equilibrium with the solid metal sulfides in the diluting drilling discharge plume before the solids settle to the sea floor or are diluted to very low concentrations. Therefore, an empirical approach is best suited for predicting the concentration of dissolved (bioavailable) metals in a drilling waste plume in the ambient water column.

Nominal barite–water distribution coefficients, K_d, for the metals of interest were determined empirically by Crecelius et al. (2007). Crecelius et al. (2007) give a detailed description of the methods used to measure dissolution of metals from several barite samples into seawater, sediment porewater, or phthalate buffers under different pH and dissolved oxygen concentration conditions. The reader is referred to Crecelius et al. (2007) for a detailed summary of the results of all dissolution experiments.

One approach to estimation of the bioavailable fraction of metals associated with drilling mud barite is to measure the solid barite–seawater distribution coefficients ($Kd_{barite–seawater}$) for metals under different pH, dissolved oxygen, and salinity conditions. Several partitioning experiments were performed with four samples of drilling mud barite, including a low trace metal barite (MI-Low), a high trace metal barite (MI-High), a laboratory blend of barites from several sources (Lab Blend), and a Norwegian drilling mud barite (NORBAR; Crecelius et al. 2007). Metals concentrations varied widely in the 4 barite samples (Table 1). Concentrations of cadmium, mercury, and zinc were the most variable. Metals concentrations in drilling mud barites usually are in the range summarized in Table 1.

Barite samples were equilibrated for 1 to 7 d with O_2-saturated natural seawater (31‰ Gulf of Mexico seawater) at a pH of 7.3 or 8.3 in experiments performed at Florida Institute of Technology (Crecelius et al. 2007). Concentrations of metals were measured in the barite samples and in the seawater at the end of the equilibration period. $Kd_{barite–seawater}$ is the concentration ratio, micrograms per gram of metal in barite (C_{barite}) divided by microgram per gram of metal in solution in water equilibrated with barite (C_{water}). Log $Kd_{barite–seawater}$ values were calculated as log C_{barite}/log $C_{seawater}$ at the end of the equilibration period.

Barium, with a very low seawater solubility, has a log $Kd_{barite–seawater}$ greater than 7 (Table 3). The high $Kd_{barite–seawater}$ values for some metals in barite are caused either by high concentrations in the solid (barite) phase (e.g., barium), or extremely low dissolved metal concentrations in the seawater phase (e.g., mercury). Metals that are present in the barite at relatively low concentrations or in the natural seawater at relatively high concentrations (e.g., cadmium and zinc, respectively) have low $Kd_{barite–seawater}$ values. The lowest log $Kd_{barite–seawater}$ value for each metal was used as the log $Kd_{barite–seawater}$ for estimating PEC in the water column within a drilling discharge plume.

The potentially bioavailable fraction of a metal in the drilling waste plume decreases as log $Kd_{barite–seawater}$ increases. Thus, cadmium and zinc are the most bioavailable metals from barite in the discharge plume, with log $Kd_{barite–seawater}$ ranging from 2.6 to 4.3 (Table 3). The log $Kd_{barite–seawater}$ of 2.6 for cadmium means that water in a discharge plume containing a high concentration of suspended barite particles contaminated with 1 μg/g cadmium might contain up to 2.5 μg/L dissolved cadmium (about 10 times the concentration of cadmium in filtered Gulf of Mexico seawater used by Crecelius et al. [2007] in their experiments). The target metals, other than barium, that leached in smallest amounts from the 3 barites are copper and mercury, the metals with the lowest K_{sp} values for their respective sulfides.

Barite grain size in these experiments ranged from 1.35 μm to 5.62 μm, so surface area of the barite in contact with seawater was high, indicating that the barite has a very low solubility in seawater. Barium solubility from barite measured in these experiments ranged from 10 to 40 μg/L, similar to the background concentration in natural seawater. The metals in barite dissolved completely in concentrated hydrochloric acid or aqua regia, but less than 0.1% of the barite dissolved, indicating that the metals were in a separate phase and not associated with the barite crystal lattice.

Trefry et al. (1986) obtained similar results in earlier studies on partitioning of metals from 4 barite samples into seawater. They showed that cadmium is the least tightly bound metal and that little barium dissolves into the seawater.

The concentration of bioavailable metals in the drilling discharge plume (the $PEC_{seawater}$) can be estimated from the log $Kd_{barite–seawater}$ values estimated here. The $PEC_{seawater}$ for metals originating from barite particles in the water column are estimated by Equation 1 (Rye 2006):

$$PEC_{seawater} = \frac{C_{discharge} \times FRACTION_{metal}}{DILUTION \times Kd_{barite-seawater}} \qquad (1)$$

in which:

$PEC_{seawater}$ = concentration in seawater of metal (mg/L)

$C_{discharge}$ = concentration of barite particles in the discharge (mg/L)

DILUTION = dilution in the recipient water predicted by a model

$FRACTION_{metal}$ = fraction of the metal in barite (kg metal/kg barite)

$Kd_{barite–seawater}$ = distribution coefficient between the metal in barite particles and dissolved metal in seawater

Table 3. Ranges of barite–seawater distribution coefficients ($Kd_{barite–seawater}$ and log $Kd_{barite–seawater}$) for metals in barite equilibrated for 1–7 d with natural seawater (salinity 31, temperature 20 °C, and pH 7.3 and 8.3). Four grades of drilling mud barite were used: MI-low, MI-high, Lab blend, and NORBAR.[a] Data are from Crecelius et al. (2007)

Metal	$Kd_{barite–seawater}$	Log $Kd_{barite–seawater}$	Log $Kd_{barite–seawater}$ applied in the water column
Barium	15000000–25000000	7.17–7.40	Not included
Cadmium	400–6000	2.60–3.78	2.6
Chromium	13000–22000	4.11–4.34	4.1
Copper	20000–80000	4.30–4.90	4.3
Mercury	300000–1300000	5.48–6.11	5.48
Lead	20000–30000	4.30–4.48	4.3
Zinc	2000–20000	3.30–4.30	3.3

[a] MI-low = low trace metal barite; MI-high = a high trace metal barite; Lab blend = a laboratory blend of barites from several sources; NORBAR = Norwegian drilling mud barite.

Input parameters to Equation 1 include, the estimated concentration of barite in the plume, the barite–seawater partition coefficient ($Kd_{barite–seawater}$) for the metal between the barite particle and metal dissolved in the seawater phase (Table 3), the modeled dilution of the waste plume, and the fraction of the metal in barite. Therefore, the $PEC_{seawater}$ for metals represents the leached fraction (dissolved) originating from the barite particles but does not consider the possibility that metals that leach from barite may rapidly adsorb to drilling waste particles, particularly clay, or suspended matter present in the water column. The lowest value of $Kd_{barite–seawater}$ in Table 3 is recommended for estimating PEC; it represents the highest potential for metal leaching to the water column. In addition, the regional background concentration ($PEC_{regional}$) of the metal should be taken into account in the local water column.

ESTIMATION OF PEC FOR METALS FROM BARITE IN SEDIMENTS

Discharged drill cuttings usually contain about 10% to 15% adsorbed drilling mud solids. Water-based drilling muds, which are the only drilling muds sometimes permitted for ocean discharge, contain 6 to more than 2000 kg barite/m^3 (US National Research Council 1983). Most of the barite and associated metals in drilling mud settle rapidly to and accumulate in bottom sediments, usually within a few kilometers of the discharge site (Neff 2005).

The solubility of barite in marine sediments and drill cuttings piles is controlled by sulfate concentration in sediment porewater (Monnin et al. 2001). As sediment oxygen is depleted by microbial degradation of organic matter, sulfate-reducing bacteria use sulfate as an alternate electron source for organic matter metabolism and generate sulfide that combines with and precipitates sediment metals (Hartley et al. 2003). If barite concentration in sediments is high, it can serve as a source of reducible sulfate for sulfate-reducing bacteria (Karnachuk et al. 2002; Ulrich et al. 2003), releasing dissolved barium into porewater (Phillips et al. 2001). Shimmield et al. (2000) showed that dissolved barium concentration increases in porewater of anoxic, sulfide-rich layers of some North Sea cuttings piles as a result of decreases in porewater sulfate through reduction by sulfate-reducing bacteria. Crecelius et al. (2007) showed that, under reducing conditions in Gulf of Mexico sediments containing barite, the concentration of dissolved barium in sediment porewater ranged from 2600 to nearly 7000 µg/L compared to a mean concentration of 45 µg/L in oxidized sediment porewater. Much of the barium released into sediment porewater by the activity of sulfate-reducing bacteria diffuses upward to the oxic layers of the sediment or into the overlying water column, where it precipitates with sulfate in the oxygenated water phase (Paytan et al. 2002). Thus, barite is highly persistent in marine sediments and drill cuttings piles.

Metals associated with sulfide minerals in the barite are nearly insoluble in suboxic marine sediment porewaters (often high in dissolved sulfide; Trefry et al. 1986; Neff 2002a, 2002b). Although chromium precipitates as the hydroxide ($Cr(OH))_3$ rather than the sulfide, little dissolves in anoxic sediment layers despite the reduction in pH of anoxic sediment porewater. Dissolution of metal sulfides from barite in sediments into sediment porewater is controlled by the concentration of reactive sulfide in the sediments. The concentration of reactive sulfide in sediment can be estimated as acid volatile sulfide, which seems to control the concentration of bioavailable metals in sediment (Ankley et al. 1991).

The surface layer is the most biologically active layer of the sediment because the oxygen concentration is higher and sulfide concentration is lower there than in deeper layers. Sediment pH varies little with changes in oxygen concentration, so pH has little effect on the solubility of barite or metal sulfides in barite. However, the pH of the gut fluids of benthic invertebrates may be low enough to enhance dissolution of small amounts of metals adsorbed to sediment iron/manganese oxyhydroxides or associated with drilling mud barite. Therefore, it is recommended that values for $Kd_{barite–porewater}$ applied to sediments should be estimated from data on sediment–water partitioning at lower pH values and/or following longer equilibration times compared to $Kd_{barite–porewater}$ values derived for the water column.

The solubility of metals from barite in acid buffer solutions (from which estimates of $Kd_{barite–porewater}$ for barium and metals in barite can be made) were estimated by Crecelius et al. (2007). Three of the 4 barite samples listed in Table 1 were equilibrated with phthalate-buffered fresh water at pH ranging from 2.3 to 6 and concentrations of 7 metals in the

Table 4. Log barite–porewater distribution coefficients (log $\mathrm{Kd}_{\text{barite–porewater}}$) for metals in 3 of the barite samples in Table 1. Barite samples were incubated in 10:1 or 4:1 dilutions of pH 3 phthalate buffer for 15 min to 48 h. $\mathrm{Kd}_{\text{barite–porewater}}$ is the concentration ratio, μg/g metal in barite/μg/g metal in solution in pH 3 buffer equilibrated with barite. Data are from Crecelius et al. (2007). The $\mathrm{Kd}_{\text{barite–porewater}}$ values recommended as sediment log K_d values are included[a]

Metal	Log $\mathrm{Kd}_{\text{barite–porewater}}$ MI-low	Log $\mathrm{Kd}_{\text{barite–porewater}}$ MI-high	Log $\mathrm{Kd}_{\text{barite–porewater}}$ Lab blend	Log $\mathrm{Kd}_{\text{barite–porewater}}$ applied to the sediments
Barium	4.62	5.30	6.27	Not included
Cadmium	0.94	1.26	1.36	0.94
Chromium	3.12	2.45	2.82	2.45
Copper	1.79	1.39	1.61	1.39
Mercury	6.94	5.31	7.58	5.31
Lead	1.88	2.97	2.28	1.88
Zinc	1.80	1.51	1.72	1.51

[a] MI-low = low trace metal barite; MI-high = a high trace metal barite; Lab blend = a laboratory blend of barites from several sources.

buffed water and solid barite were measured after different equilibration times (Table 4). These data can be used to estimate log $\mathrm{Kd}_{\text{barite–porewater}}$ for the selected metals between the barite particle and porewater in the sediments.

The pH of most marine sediments rarely drops below about 6. Fluids in the digestive tract of benthic, sediment-ingesting invertebrates usually have a pH of 5 to 6; fish digestive fluids may be somewhat more acidic. Log $\mathrm{Kd}_{\text{barite–porewater}}$ decreased with decreasing pH for most metals in the 3 barites. This indicates that the solubility and potential bioavailability of metals in barite are highest (i.e., lowest log $\mathrm{Kd}_{\text{barite–porewater}}$ values) at low pH and decrease as pH increases (i.e., highest log $\mathrm{Kd}_{\text{barite–porewater}}$ values). Therefore, the conservative $\mathrm{Kd}_{\text{barite–porewater}}$ values obtained at pH of 3 are recommended for calculation of PEC for metals in barite for the sediments, to take into account possible enhanced extraction of metals from barite in the dilute acid environment of the digestive tract of benthic or demersal invertebrates and fish.

Log $\mathrm{Kd}_{\text{barite–porewater}}$ is below 2 for cadmium, copper (except at a pH of 6), and zinc for all 3 barites at all pH between 2.3 and 6. A log $\mathrm{Kd}_{\text{barite–porewater}}$ of 2 indicates that the concentration of the metal is 100 × higher in the barite than in the porewater in equilibrium with the barite. For example, the concentration of cadmium in the pH 3 buffer equilibrated with the laboratory blend barite (containing 7 mg/kg cadmium) is 0.32 mg/L (the log $\mathrm{Kd}_{\text{barite–porewater}}$ is 1.36 at pH 3). These results indicate that cadmium, copper, lead, and zinc are the metals in drilling mud barite with the greatest potential to leach from drilling mud barite into sediment porewater and gut fluids and bioaccumulate in benthic animals from ingestion of mud/cuttings in seafloor sediments.

The log $\mathrm{Kd}_{\text{barite–porewater}}$ values for mercury in the 2 barite samples containing the highest concentrations of mercury (MI-High and Lab Blend) were high and did not vary much with pH (log $\mathrm{Kd}_{\text{barite–porewater}}$ for MI-High, 5.25–5.77; log $\mathrm{Kd}_{\text{barite–porewater}}$ for Lab Blend, 7.48–7.78). Mercury has the highest log $\mathrm{Kd}_{\text{barite–porewater}}$ values of the metals examined, because of the low K_{sp} of mercuric sulfide (Table 2) and because concentrations of mercury in the barite samples were lower than those for the other metals, particularly in the low trace metal barite, typical of the drilling mud barite used offshore in the Gulf of Mexico and North Sea (Table 1).

The $\mathrm{Kd}_{\text{barite–porewater}}$ values summarized in Table 4 can be used to predict $\mathrm{PEC}_{\text{sediment}}$ for drilling mud metals in sediments and cuttings piles. $\mathrm{PEC}_{\text{sediment}}$ is estimated by Equation 2:

$$\mathrm{PEC}_{\text{sediment}} = \frac{C_{\text{sediment}} \times \mathrm{FRACTION}_{\text{metal}}}{\mathrm{Kd}_{\text{barite-porewater}}} \tag{2}$$

in which:

$\mathrm{PEC}_{\text{sediment}}$ = concentration of bioavailable metal in sediment (mg/L)

C_{sediment} = concentration of barite in sediment (barite concentration = 1.7 times barium concentration)

$\mathrm{FRACTION}_{\text{metal}}$ = fraction metal in barite (kg metal/kg barite)

$\mathrm{Kd}_{\text{barite–porewater}}$ = distribution coefficient between metal in barite and dissolved metal in sediment porewater

Crecelius et al. (2007) evaluated dissolution of barium and metals from different grades of barite mixed with oxic and anoxic sediments. Concentrations of dissolved lead and zinc increased in porewater of oxidizing sediment layers containing the lab blend (high in metals) barite after several months of incubation. Concentrations of barium and the other metals did not increase, indicating that they had a very low solubility in oxidized layers of sediment.

Small amounts of barium and zinc dissolved in porewater of anoxic sediment containing a high trace metal barite after several months of incubation. Concentrations of cadmium, chromium, copper, mercury, methylmercury, and lead did not change, indicating that these metals were not soluble in the porewater of anoxic sediments. The absence of methylmercury confirms the observation of Trefry et al. (2007) that mercury in barite is not converted to methyl mercury by sulfate-reducing bacteria in anoxic sediment layers. These results indicate that only lead and zinc may dissolve from a high trace metal barite into sediment porewater. There would be little or no dissolution of metals from modern low trace metal barites.

Because the cuttings pile on the sea floor usually is enriched in biodegradable organic matter (Hartley et al. 2003; Neff 2005), primarily from drilling mud adhering to the cuttings particles, much of the metals dissolving from drilling mud barite into porewater will complex rapidly with dissolved and particulate organic matter in the porewater, reducing their bioavailability to sediment-dwelling animals. Thus, $\mathrm{PEC}_{\text{sediment}}$

Table 5. Metals concentrations in 7 samples of Italian water-based drilling muds (WBM), in a 0.5 M acetic acid (HAc) extract of the muds, and resulting K_d and log K_d values. Concentrations are mg/kg in sediment and mg/L in water. Data are from Terzaghi et al. (1998). FW = freshwater; SW = seawater

Metal and drilling mud	Mud (mg/kg)	HAc (mg/L)	K_d	Log K_d
Cadmium				
FW-gel	0.12	0.0009	133	2.12
FW-gel-lignosulfonate	0.13	0.001	130	2.11
FW-lignosulfonate	0.05	0.0009	56	1.74
FW-lignosulfonate-Soltex	0.03	0.0007	43	1.63
FW-polymer	1.06	0.0011	964	2.98
SW-polymer	0.11	0.0021	52	1.72
FW-Mor-Rex	0.02	0.0006	33	1.52
Chromium				
FW-gel	3.66	0.0039	938	2.97
FW-gel-lignosulfonate	1064	10.156	105	2.02
FW-lignosulfonate	662	6.923	96	1.98
FW-lignosulfonate-Soltex	325	3.849	84	1.93
FW-polymer	4.62	0.0372	124	2.09
SW-polymer	2.99	0.0214	140	2.15
FW-Mor-Rex	4.08	0.0299	136	2.13
Copper				
FW-gel	3.13	0.0011	2845	3.45
FW-gel-lignosulfonate	3.2	0.0362	88	1.95
FW-lignosulfonate	5.81	0.0906	64	1.81
FW-lignosulfonate-Soltex	4.89	0.0446	110	2.04
FW-polymer	3.68	0.0551	67	1.82
SW-polymer	1.96	0.0479	41	1.61
FW-Mor-Rex	0.87	0.0176	49	1.69
Lead				
FW-gel	0.21	0.0038	55	1.74
FW-gel-lignosulfonate	0.19	0.0015	127	2.10
FW-lignosulfonate	0.23	0.0025	92	1.96
FW-lignosulfonate-Soltex	0.43	0.0006	717	2.86
FW-polymer	0.23	0.0004	575	2.76
SW-polymer	0.19	0.0019	100	2.00
FW-Mor-Rex	0.42	0.0005	840	2.92

for different barite metals estimated from $Kd_{\text{barite–porewater}}$ by Equation 2, are conservative estimates.

Terzaghi et al. (1998) measured the concentration of 5 metals (arsenic, cadmium, chromium, copper, and lead) in 0.5 M acetic acid extracts (i.e., the exchangeable fraction) of 7 samples of WBM used in Italian drilling operations in the Mediterranean Sea. They estimated K_d values that were remarkably similar to those reported here. Only chromium had a lower K_d in whole drilling mud than in barite. This is because chromium often is added to WBM in clay thinners, such as chrome lignosulfonate, which are moderately water-soluble (Neff et al. 1987). These data also can be used to derive K_d values for the metals in drilling wastes on the sea floor.

Log K_d values from Terzaghi et al. (1998) data indicate that only a small fraction of the metals associated with the typical WBMs is in the exchangeable, readily bioavailable fraction of the drilling muds. Log K_d values range from 1.63 (cadmium in freshwater–lignosulfonate–Soltex mud) to 3.45 (copper in

Table 6. Summary of recommended K_d values for estimation of predicted environmental concentrations (PEC) of metals from drilling mud barite in the water column or marine sediments, compared to the log K_d values for the metals in Italian water-based drilling muds (WBM)

Metal	Log $Kd_{barite–seawater}$ (water)	Log $Kd_{barite–porewater}$ (sediment)	WBM log K_d
Cadmium	2.6	0.94	1.6–3.0
Chromium	4.1	2.4	1.9–3.0
Copper	4.3	1.4	1.6–3.4
Mercury	5.5	5.3	NV[a]
Lead	4.3	1.9	1.7–2.9
Zinc	3.3	1.5	NV

[a] NV = no value.

freshwater–gel mud; Table 5). The log K_d values from the Terzaghi et al. (1998) data approximate estimates of the bioavailable fraction of metals from whole drilling muds. However, if the cuttings contain a large fraction of organic matter, clay, or water-sensitive shales, much of the metal desorbing from the mud will rapidly adsorb to the organic matter or clay mineral fraction of the cuttings, decreasing metal bioavailability.

The similarity of log K_d values for metals, except chromium, in barite and whole WBM confirm that the potentially bioavailable fraction of metals in whole WBM is associated primarily with the barite fraction in the mud. Water-based drilling muds used at the time of the Terzaghi et al. (1998) study sometimes contained chromium in the form of chrome lignosulfonates, added as clay deflocculents (Neff 2005). Chrome lignosulfonates are water-soluble and undoubtedly contribute to the bioavailable fraction of chromium in WBMs that contain them.

SUMMARY AND CONCLUSIONS

The metals in drilling mud barite are associated with metal sulfide (sphalerite and pyrite) inclusions in the solid barite. Release of dissolved metals from solid barite depends on the solubility products of the metal sulfides, and is not an equilibrium partitioning process between adsorbed, exchangeable metals and dissolved metals. Thus, an empirical approach was adopted for estimating the concentration of dissolved metals (the PEC) released from solid barite in a drilling mud or drill cuttings plume in the water column or in porewater of sediments containing solid barite in drilling mud or cuttings.

Nominal barite–water distribution coefficients ($Kd_{barite–seawater}$) for the water column were estimated from results of laboratory dissolution experiments in which different grades of drilling mud barite were equilibrated with natural seawater (Crecelius et al. 2007). Nominal distribution coefficients were estimated as the ratio of the metal concentration in the barite to its concentration in the seawater in which the barite was dispersed. Nominal barite–porewater distribution coefficients for sediments were estimated as the ratio of the metal concentration in barite to its concentration in a pH 3 phthalate buffer. This approach was intended to simulate the dissolution of barite in the digestive tract of a deposit-feeding benthic invertebrate or demersal fish.

The log $Kd_{barite–seawater}$ values for metals in the water column were higher than log $Kd_{barite–porewater}$ values for metals in sediment porewater (or digestive tract fluids of benthic animals; Table 6). Thus, the metals in barite are less bioavailable in the water column than in the digestive tract of a benthic animal. This reflects the fact that metal sulfides are more soluble in acid (digestive fluid) than in alkaline (seawater) fluids.

The $Kd_{barite–porewater}$ values for sediment estimated as described above were compared to K_d values estimated by extracting whole drilling muds with weak acid (Terzaghi et al. 1998). The log K_d values for drilling muds were similar to those estimated here for sediments, indicating that little of the metals in WBM are in readily exchangeable forms. The exception is chromium, which may be present in WBM as soluble chrome lignosulfonate clay deflocculent.

The log K_d values derived in this paper were used by Altin et al. (2008) and Rye et al. (2008) with data on concentrations of barite in the drilling mud/cuttings plume and in bottom sediments to calculate $PEC_{seawater}$ and $PEC_{sediment}$ for the metals in drilling mud barite. These PEC values were then used in an environmental risk assessment for drilling discharges.

Guidance for preparing environmental risk assessments for chemical discharges to European waters is provided in the European Union Technical Guidance Document (EC 2003). According to the Technical Guidance Document, environmental risks for chemicals are estimated by calculation of PEC–PNEC ratios. The PEC is an estimate of the concentration of a chemical to which the biota are exposed during and after discharge of the chemical. The PNEC is the concentration of the chemical in the environment below which it is unlikely that adverse effects on the biota will be observed.

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