
Barium in Produced Water: Fate and Effects in the Marine Environment

Health and Environmental Sciences Department
Publication Number 4633
September 1995

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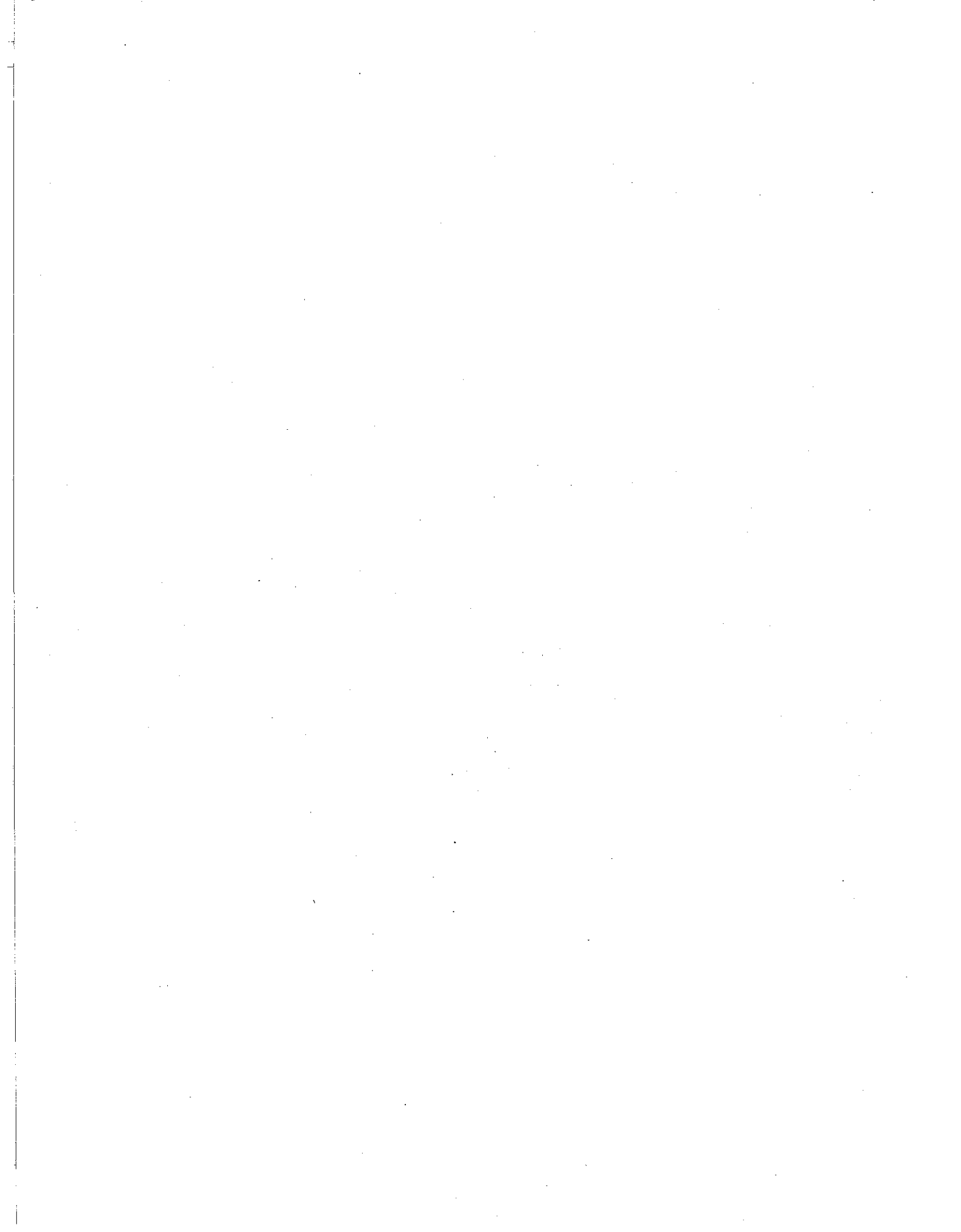
API PUBLICATION NUMBER 4633

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APRIL 1995

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ACKNOWLEDGMENTS

THE FOLLOWING PEOPLE ARE RECOGNIZED FOR THEIR CONTRIBUTIONS OF TIME AND EXPERTISE DURING THIS STUDY AND IN THE PREPARATION OF THIS REPORT:

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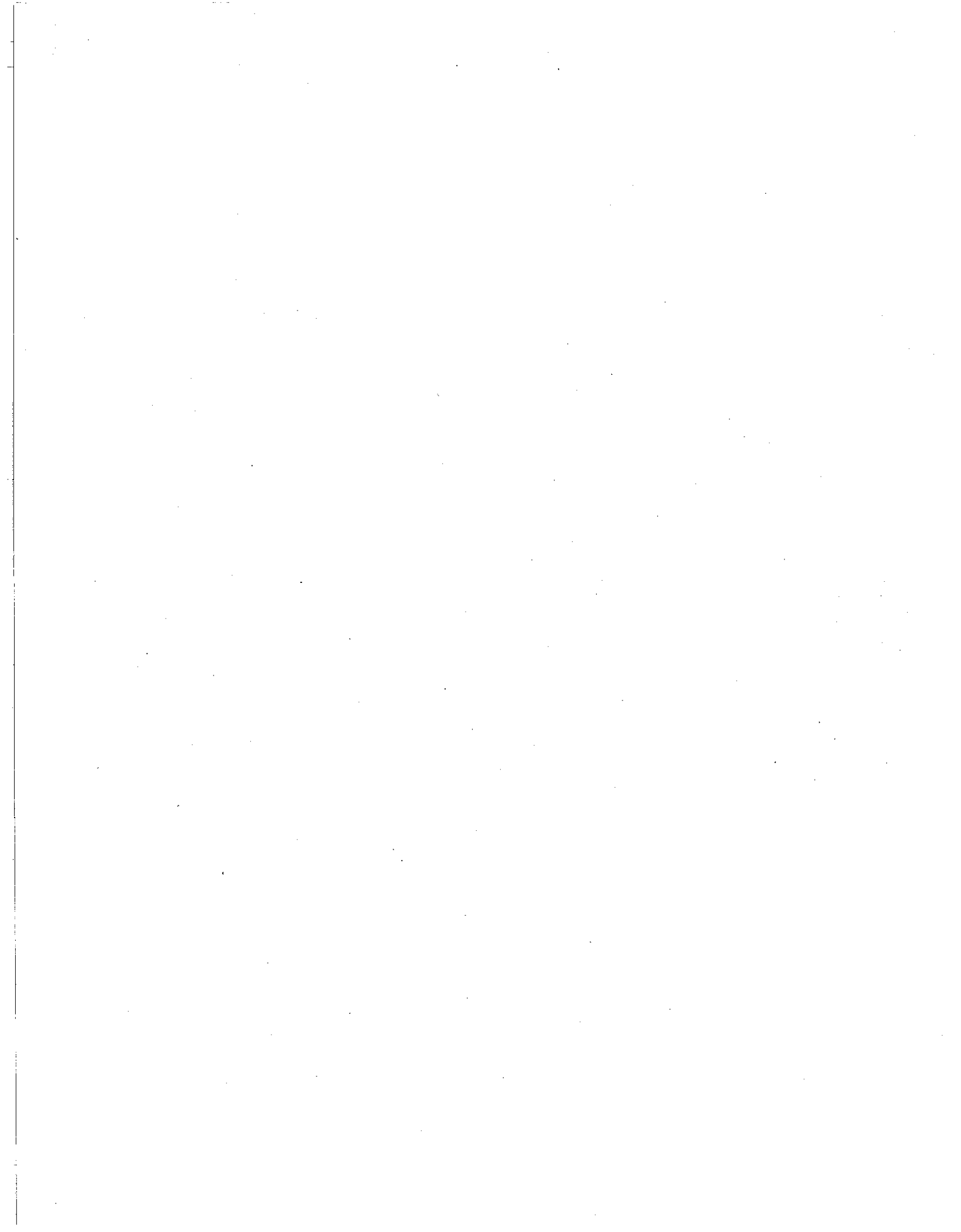
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EXECUTIVE SUMMARY

This review provides a summary of what is currently known about the physical/chemical behavior of barium in produced water and in the ocean and discusses the factors that may influence the rate of precipitation of barium as barite. The toxicity of barium to marine and freshwater organisms and humans also is discussed in relation to the concentrations and forms in which barium may occur in the marine and aquatic environment.

The concentration of dissolved barium in oil well produced water ranges from less than 100 to more than 2,000,000 $\mu\text{g/L}$ (parts per billion). The concentration of dissolved barium in the ocean is in the range of 4 to about 20 $\mu\text{g/L}$ and is controlled by the high concentration of sulfate in sea water. Barium sulfate (barite) has a low aqueous solubility, reflected by its molal solubility product of approximately 1.05×10^{-10} at 25°C. The saturation concentration of barium in equilibrium with barite in sea water is approximately 37 $\mu\text{g/L}$. Consequently, it is expected that when produced water containing a high concentration of dissolved barium is discharged to the ocean, the barium will precipitate rapidly as barite. However, organic acid anions, sometimes present in produced water at concentrations as high as 10,000,000 $\mu\text{g/L}$, may complex with barium and slow its precipitation upon mixing of produced water with seawater.

Barium concentrations in produced water are roughly inversely proportional to concentrations of sulfate, indicating that the barium is in equilibrium with barite in the formation. If saline water is injected into the fossil fuel reservoir to enhance secondary production and some of the injection water mixes with the formation water, the concentration of sulfate in the produced water may cause supersaturation with respect to barite.

The rate of precipitation of barium from produced water in the ocean has not been measured directly. Upon discharge of produced water to the ocean, precipitation of barium as barite may be slow unless the produced water/sea water mixture is several-fold supersaturated with respect to free, ionic Ba^{+2} and SO_4^{-2} . After initial barite crystal nuclei are formed, precipitation may be rapid. Produced water containing more than about 100 $\mu\text{g/L}$ dissolved barium will produce, upon discharge, a produced water/sea water mixture that is supersaturated with respect to barite in the presence of a typical concentration of sulfate in sea water (0.028 M).

A typical Gulf of Mexico produced water contains about 50,000 $\mu\text{g/L}$ (0.000364 M) dissolved barium; Gulf of Mexico sea water contains about 0.029 M sulfate. Assuming an apparent activity coefficient of 0.2 for barium in produced water and an apparent activity coefficient of 0.17 for sulfate in sea water, a 99:1 sea water:produced water mixture is about 30 times supersaturated with respect to barite. The rate of precipitation of barite from such a highly supersaturated mixture is diffusion-rate limited, so precipitation will be very rapid in a well-mixed receiving water environment.

If a scale inhibitor is used in the production stream or produced water treatment system, it may appear in the treated produced water that is discharged to the ocean and may inhibit the initiation or slow the rate of precipitation of barium. In addition, organic acid anions, sometimes present at high concentrations in produced water, may complex with dissolved barium, reducing its apparent activity coefficient and reducing the rate of barium precipitation in the ocean.

Solid barite and dissolved barium in sea water are not very toxic to marine and freshwater organisms. In sea water, toxic concentrations of barium ion are in excess of barium solubility and are only observed in bioassays with embryos and larvae of marine invertebrates during exposure to fine suspended barite particles or

barium-organic acid complexes. In fresh water, barium solubility is controlled by sulfate; barium can only reach toxic concentrations if the water contains a low concentration of sulfate. Barium in drinking water has a low toxicity to humans. Thus, dissolved barium at concentrations that are stable in the sea water and fresh water is not likely to be toxic to marine, freshwater, or terrestrial organisms.



Section 1 INTRODUCTION

The two most important (in terms of volumes generated and regulatory concern) waste products sometimes permitted for discharge from offshore exploration and production platforms are drilling fluids and produced water (Neff *et al.*, 1987). Both wastes are complex mixtures of water-soluble and insoluble, inorganic and organic chemicals in water. Barium is one of the most abundant inorganic chemicals (other than the dominant seawater ions) in both drilling fluids and produced water from some locations. Barium is added intentionally, as the mineral barium sulfate (BaSO_4), to most drilling fluids as a weighting agent because of its high density and low aqueous solubility. Barium is a natural ingredient of produced water.

Studies of barite in drilling fluids generally have shown that this dense, insoluble mineral is virtually nontoxic to marine organisms (National Research Council, 1983). The low toxicity of barite to marine organisms usually is attributed to its low solubility in seawater (high in sulfate). However, most of the barium in produced water is present in a dissolved form. Concern has been expressed and some circumstantial evidence published (Higashi *et al.*, 1992; Raimondi and Schmitt, 1992; Cherr and Fan, 1993) that dissolved or colloidal barium discharged to the sea in produced water may be toxic to sensitive life stages of marine organisms. The kinetics of precipitation of soluble barium as barite upon mixing of produced water with sea water is not understood; therefore, the persistence of dissolved barium in a diluting produced water plume at concentrations significantly higher than natural background is not known.

The objectives of this review are to summarize the scientific literature on the concentrations and behavior of barium in produced water and its behavior and

toxicity upon discharge to saline receiving waters. The concentrations and chemical speciation of barium in natural marine and fresh water and in produced water are discussed first. This section will include a discussion of the effects of various physical and chemical parameters on the solubility product of barite and the solubility of barium. Our current understanding of the physical chemistry of precipitation of barium upon mixing of produced water with sea water is described next. There is a discussion of the factors that may affect the rate of barium precipitation following discharge of produced water to the ocean. Finally, the toxicity of barium and barium sulfate to freshwater and marine organisms and humans is discussed in relation to the predicted precipitation kinetics of barium plus sulfate in the receiving water environment.

Section 2

PHYSICAL CHEMICAL PROPERTIES OF BARIUM

Barium is an alkaline earth element (Group IIA of the periodic table). There are four alkaline earths with lower molecular weights than barium. These are beryllium (MW 9.01), magnesium (MW 24.32), calcium (MW 40.08), and strontium (MW 87.63). There is one alkaline earth element with a higher molecular weight, radium (MW 226.05) (Table 2-1). Barium, with a molecular weight of 137.36, shares many physical/chemical properties with the other alkaline earth elements. Beryllium, with a charge density more than twice that of the other Group IIA elements, has different chemical properties than the other elements in the group.

Table 2-1. Physical/Chemical Properties of the Alkaline Earth Elements (Group IIA). From Snavely (1989).

Ion	Molecular Weight	Crystal Radius (Å)	Hydrated Radius (Å)	Charge Density	K_{sp} [M][SO ₄] @ 25°C
Be ⁺⁺	9.01	0.31	4.59	6.45	--
Mg ⁺⁺	24.32	0.65	4.28	3.01	--
Ca ⁺⁺	40.08	0.99	4.12	2.02	3.75X10 ⁻⁵
Sr ⁺⁺	87.63	1.13	4.12	1.77	3.42X10 ⁻⁷
Ba ⁺⁺	137.36	1.35	4.04	1.48	1.05X10 ⁻¹⁰
Ra ⁺⁺	226.05	1.52	3.98	1.32	4.30X10 ⁻¹¹

Like all the alkaline earth elements, barium readily loses its outer two electrons, forming the divalent cation (Ba⁺²). Barium is a stronger reducing agent and more readily forms bases than the other alkaline earths, except radium. Because barium has a relatively low ionic potential, it goes into aqueous solution as the hydrated ion. Adsorption of ionic barium to clay particles and organic matter is stronger

than adsorption of lower molecular alkaline weight earths, because of its smaller hydrated ionic radius (Lagas *et al.*, 1984).

All the alkaline earth elements readily form oxides, hydroxides, carbonates, and sulfates. However, because its crystal radius (1.35 Å) is larger than that of lower molecular weight alkaline earths, Ba⁺² does not readily substitute for other alkaline earths in various crystal matrices, such as calcium carbonate. Barium is incorporated more readily into precipitating calcite than aragonite (Kitano *et al.*, 1971); it also tends to inhibit incorporation of strontium into these two crystal forms of calcium carbonate (Morse and Bender, 1990). The most abundant naturally occurring barium minerals are barite (BaSO₄; also called barytes), witherite (BaCO₃), barytoangelsite ([Ba,Pb]SO₄), and bromlite (CaBa[CO₃]) (Pilkey, 1972).

Barium, like the other alkaline earth elements, forms soluble salts with chloride, bromide, and nitrate, and relatively insoluble salts with sulfate, carbonate, phosphate, and acid phosphate. The least soluble barium salt is barite with a solubility product (K_{sp}) of approximately 1.05×10^{-10} at atmospheric pressure and a temperature of 25°C (Table 2-1). Barite has a low solubility in fresh water and sea water of 2,300 µg/L (1,360 µg Ba/L) and 81 µg/L (48 µg Ba/L), respectively, at 20°C (Burton *et al.*, 1968). The solubility product increases with temperature, resulting in barite solubilities in distilled water ranging from 1,746 µg/L (1,027 µg Ba/L) at 0°C to 3,946 µg/L (2,320 µg Ba/L) at 100°C (Haarberg *et al.*, 1992). The solubility product of barite also increases with increasing ionic strength of the water. At 25°C, the solubility of barite increases from approximately 2,450 µg/L (1,441 µg Ba/L) in deionized water to 25,680 µg/L (15,100 µg Ba/L) in water with an ionic strength of 1.4 molal as various inorganic chlorides (Haarberg *et al.*, 1992). At the ionic strength of sea water (≈ 0.66 M with respect to NaCl), barite would have a solubility of 15,400 µg/L (9,060 µg Ba/L) in the absence of sulfate. However, the high concentration of inorganic sulfate in sea water controls the solubility of barite and the saturation concentration of dissolved barium at a much lower level.

Section 3

BARIUM IN PRODUCED WATER AND NATURAL WATERS

BARIUM IN PRODUCED WATER

Water may be trapped with liquid and gaseous petroleum during millions of years of geologic time in porous sediments sandwiched between layers of impermeable rock deep within the earth. This water, called formation water or produced water, may be generated with the fossil fuels. Freshwater or seawater may be injected into the hydrocarbon reservoir to increase production of fossil fuels. Some of this injected water may mix with and be produced with the formation water. Water generated during fossil fuel production from offshore oil and gas reservoirs often is treated to remove as much oil as possible and discharged to the sea.

Large amounts of treated produced water are discharged to the ocean each year.

Table 3-1 summarizes the volumes discharged in several major offshore oil and gas production areas world-wide.

Table 3-1. Estimated Average Volumes in Millions of Liters/Day (Millions of Barrels/Day in Parentheses) of Treated Produced Water Discharged to Coastal and Offshore Waters of the Gulf of Mexico, California, Cook Inlet, Alaska, the North Sea, and Australia.

Location	Average Daily Discharge	Reference
Gulf of Mexico	547 (3.44)	Boesch and Rabalais, 1989a
California	140 (0.88)	Hudgins, 1992
Cook Inlet, AK	15 (0.09)	Neff, 1991
North Sea	450 (2.83)	Bedborough <i>et al.</i> , 1987
Australia	100 (0.63)	Black <i>et al.</i> , 1994

Most discharges of treated produced water from individual oil/water separator or production platforms to nearshore waters of the northwestern Gulf of Mexico are less than about 80,000 L/d (500 bbl/d) (Boesch and Rabalais, 1989a). Large production or treatment facilities may discharge much larger volumes of treated produced water. The Grand Isle treatment facility, which no longer discharges produced water, received produced water from several offshore fields in the northern Gulf of Mexico and discharged about 16.6 million L/d (104,000 bbl/d) of treated produced water to Bayou Rigaud, Louisiana in 1989 (Boesch and Rabalais, 1989a). In 1992, the Statfjord oil field, the largest offshore oil field in the world, discharged 30.9 million L/d (195,000 bbl/d) of treated produced water to the Norwegian sector of the North Sea (Ynnesdal and Furuholt, 1994).

Over the life of a well, the amount of water produced with the oil or gas often increases as the amount of fossil fuels produced decreases (Read, 1978). In older fields and stripper wells, the water fraction may be 90 percent or more. For example, produced water discharges to the Norwegian sector of the North Sea are expected to increase nearly six-fold from 43.8 million L/d in 1990 to 246.6 million L/d in the year 2000 (Brendehaug *et al.*, 1993).

Produced water is a complex mixture of a great many chemicals that have been dissolved or dispersed from the geologic formation in which the produced water resided for millions of years (Table 3-2). The most abundant organic chemicals in produced water are low molecular weight organic acids and saturated and aromatic hydrocarbons. Hydrocarbons and organic acids usually represent more than 90 percent of the organic compounds in produced water. In the United States, the current standard for total petroleum hydrocarbons (oil and grease) in treated oil well produced water destined for ocean disposal is 42 mg/L (parts per million: ppm)

Table 3-2. Typical concentration ranges of several classes of organic compounds and inorganic ions in produced water. Concentrations are in $\mu\text{g/L}$ (Parts per Billion). Data are from Kharaka *et al.*, (1978), Grahl-Nielsen (1987), McGowan and Surdam (1988), Boesch *et al.*, (1989a,b), Macpherson (1989), Barth (1991), Stueber and Walter (1991), Jacobs *et al.*, (1992), Neff *et al.*, (1992), Stephenson (1991, 1992), and Tibbetts *et al.*, (1992).

Compound Class	Concentration Range
<u>Organic Compounds</u>	
Total Organic Carbon	< 100 - 1,500,000
Total Saturated Hydrocarbons	17,000 - 30,000
Total BTEX	300 - 93,000
Total PAH	80 - 1,700
Steranes/Triterpanes	140 - 175
Ketones	1,000 - 2,000
Phenols	600 - 2,900
Organic Acids	500 - 10,000,000
<u>Inorganic Ions</u>	
Sulfate	< 1,000 - 8,000,000
Arsenic	5 - 300
Barium	< 100 - 2,000,000
Cadmium	0.1 - 200
Chromium	0.7 - 1,100
Copper	0.4 - 1,500
Lead	1.5 - 8,800
Mercury	0.05 - 2.0
Nickel	0.4 - 1,700
Silver	12 - 152
Zinc	100 - 69,000

daily maximum and 29 ppm monthly average. Oil/water separators on offshore platforms generally are able to remove dispersed oil droplets from produced water to attain oil concentrations in the discharged produced water that are below the current standards.

Organic acid anions may be present in produced water at non-detectable concentrations ranging from zero to as high as 10,000,000 $\mu\text{g/L}$ (parts per billion) (McGowan and Surdam, 1988; Barth, 1991; Helgeson *et al.*, 1993). Most of the organic acids in produced water are short-chain aliphatic mono- and di-carboxylic acids. They are thought to have been produced by hydrous pyrolysis of hydrocarbons in the hydrocarbon-bearing formation (Borgund and Barth, 1994). The most abundant acid usually is acetic acid, though, in some coal-associated waters, propionic acid may be most abundant (Fisher, 1987).

If heavy use is made of water-soluble organic additives (e.g., biocides, scale inhibitors, anti-corrosion chemicals, flocculents) in the production stream or produced water treatment system, small amounts of them may also be present in the produced water discharged over board (Hudgins, 1989, 1991, 1992). An estimated 0.4 to 4 percent of the corrosion inhibitors, 50 to 80 percent of the flocculents, and less than 1 percent of the biocides used on production platforms in the Norwegian sector of the North Sea are discharged to the North Sea in produced water (Ynnesdal and Furuholt, 1994).

The concentration of total dissolved solids (salinity) in produced water varies widely from essentially fresh water (less than 3 ‰) to a saturated brine with a concentration of about 300 ‰ (Rittenhouse *et al.*, 1969; Large, 1990). Low salinity produced waters may have been derived from ancient freshwater lakes. However, most produced waters have salinities similar to or greater than that of sea water (salinity, about 35 ‰) and are thought to have been derived from ancient seawater (Collins, 1975). As in sea water, the dominant inorganic ions are sodium and chloride. The other abundant inorganic ions in sea water usually are present at high concentrations in saline produced waters; however, ion ratios in produced water may be different from those in modern sea water, possibly reflecting ion ratios of ancient seas.

All the alkaline earth elements, including barium, are present in most saline produced waters at much higher concentrations than in modern seawater. The concentration of barium in produced water varies from less than 100 $\mu\text{g/L}$ (Barth, 1991; Stueber and Walter, 1991) to approximately 2,000,000 $\mu\text{g/L}$ (Barth *et al.*, 1989; Macpherson, 1989). Most formation waters contain no or low concentrations of sulfur, most of it in the form of reduced sulfur species such as sulfide (Shock and Koretsky, 1993). Often, when high concentrations of sulfate are present, it is an indication of contamination of formation water with saline injection water (Barth *et al.*, 1989; Tibbetts, 1991). When both barium and sulfate are present in produced water, they may precipitate on the walls of production pipe as barium scale (barite). Therefore, concentrations of barium in the produced water in the formation may be higher than concentrations in the water that is produced, treated, and discharged to the ocean (Rollheim *et al.*, 1993).

There is a roughly inverse relationship between the concentrations of barium and sulfate in produced water (Figure 3-1). Produced waters with very high barium concentrations nearly always contain undetectable or trace concentrations of sulfate (Barth *et al.*, 1989). However, the correlation is not good, particularly for waters with low concentrations of barium. Treated produced water often contains water from other sources than the fossil formation water (e.g., saline injection water) that may contain elevated concentrations of sulfate (McCort and Peers, 1987). Barium may precipitate in water-flooded formations or in the production stream as the sulfate, so that the concentrations of barium and sulfate in such produced waters do not reflect the concentrations in the original formation water before saline water injection. However, most data fall near the $\text{Ba}^{+2}/\text{SO}_4^{-2}$ regression line for equilibrium with barite at 100°C, a typical temperature for produced water coming from a geologic formation (Macpherson, 1989). The barium in produced water probably is derived from dissolution of potassium feldspars (containing up to about 1 weight percent barium), plagioclase, and biotite

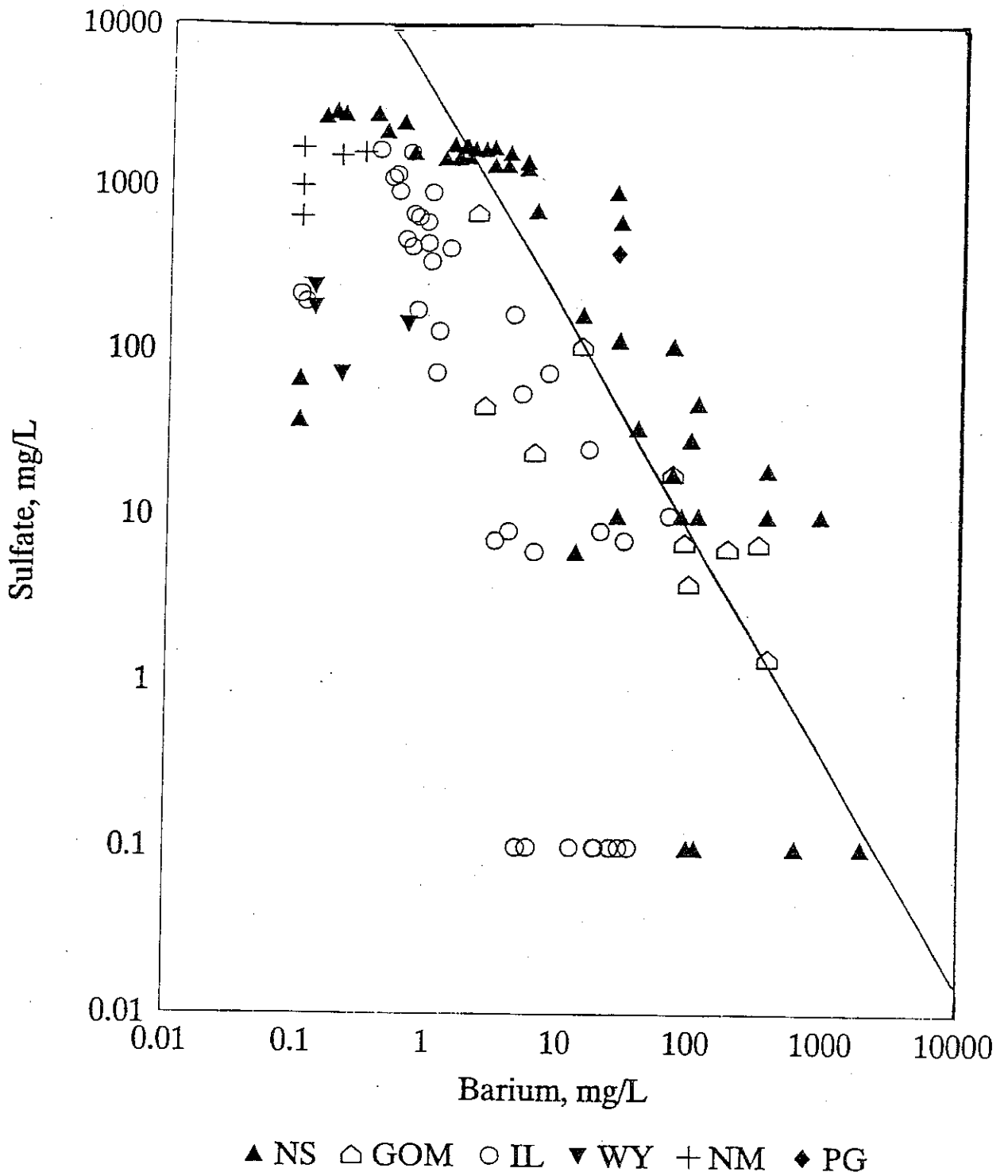


Figure 3-1. The relationship between the concentrations of barium and sulfate in produced waters from different sources. The solid line is the approximate solubility product for barite at 1000°C. NS, North Sea; GOM, Gulf of Mexico; IL, Illinois; WY, Wyoming; NM, New Mexico; PG, Persian Gulf.

in the geologic formation (Bloch and Key, 1981; Macpherson, 1989). However, its concentration probably is controlled by barite in the sandstone formation (Macpherson, 1989).

In the data on produced water composition used in Figure 3-1, concentrations of barium ranged from less than 100 $\mu\text{g/L}$ (7.3×10^{-7} M) to 1,923,000 $\mu\text{g/L}$ (0.014 M). Sulfate concentrations ranged from less than 100 $\mu\text{g/L}$ (1×10^{-6} M) to 3,015,000 $\mu\text{g/L}$ (0.03 M). Ion products for barium and sulfate in produced water are as high as 6×10^{-3} , more than 100,000-fold higher than the solubility product for barium sulfate (1.05×10^{-10} at 25°C), assuming activities in solution of about 1 for both barium and sulfate ions. Activity coefficients for Ba^{+2} and SO_4^{-2} in hot, geopressured brines are substantially lower than 1, which increases the apparent solubility of BaSO_4 (Haarberg *et al.*, 1992).

In addition, the solubility product of barite increases with increasing temperature, pressure, and ionic strength of the water (Blount, 1967; Church, 1970). This can be shown, using the example of the solubility behavior of barite in sea water. The increase in K_{sp} in saline water is about 1.8-fold between standard temperature and pressure and a temperature 100°C and a pressure of 400 bars (Haarberg *et al.*, 1992). Church and Wolgemuth (1972) estimated that the solubility of barium in equilibrium with barite increases from 24 $\mu\text{g/L}$ sea water at 1°C and 1 atm to 49 $\mu\text{g/L}$ at 1°C and 500 atm and 35 $\mu\text{g/kg}$ at 25°C and 1 atm. This may, in part, explain the high concentrations of dissolved barium in the presence of elevated concentrations of inorganic, reduced sulfur (though usually not as high as concentrations in seawater) in hot, geopressured formation and geothermal waters. In the absence of free inorganic sulfate, the solubility of barium is very high in hot, geopressured formation waters containing high concentrations of dissolved ions. This solubility behavior also explains the precipitation of barite scale in oil well production pipe as the temperature and pressure of the produced water decrease.

Produced water samples containing the highest concentrations of sulfate (e.g., samples from platforms Murchison and Hutton in the North Sea) may contain substantial additions of seawater (Tibbetts, 1991) and possibly also scale inhibitors, explaining the extreme supersaturation of some of these samples with respect to barium sulfate.

Most produced waters containing elevated concentrations of barium contain elevated concentrations of strontium as well (Kharaka *et al.*, 1978; McCort and Peers, 1987; Barth, 1991; Stueber and Walter, 1991). Strontium also forms an insoluble salt with sulfate ($[\text{Sr}][\text{SO}_4]$: solubility product at 25°C, 3.42×10^{-7}) and strong $(\text{Ba}, \text{Sr})\text{SO}_4$ complexes with barium sulfate, decreasing the activity of sulfate and the apparent equilibrium concentration of barium (Hanor, 1969; Felmy *et al.*, 1993).

BARIUM IN SEA WATER

A few attempts have been made to estimate the solubility of barium in sea water. Estimates are made difficult by uncertainties about activity coefficients for free Ba^{+2} and SO_4^{-2} in the complex ionic environment of sea water (Church, 1970, 1979; Church and Wolgemuth, 1972; Millero and Hawke, 1992). At 25°C and 1 atm, the solubility of barite in sea water is in the range of 37 to 51.7 $\mu\text{g Ba/L}$ (36.2 to 50.5 $\mu\text{g/kg}$) (Chow and Goldberg, 1960; Church, 1970). Burton *et al.*, (1968) measured a solubility of 48 $\mu\text{g/L}$ barium for barite in water from the English Channel. The estimate of Chow and Goldberg (1960) of 51.7 $\mu\text{g/L}$ total dissolved barium included 2.7 $\mu\text{g/L}$ of undissociated BaSO_4 in solution. An estimate by Desai *et al.*, (1969) of 132.3 $\mu\text{g/L}$ barium in solution in sea water in equilibrium with barite seems too high by a factor of more than 2. Barite solubility in sea water increases with increasing temperature and depth (pressure) in the ocean (Chow and Goldberg, 1960; Templeton, 1960; Church, 1970; Church and Wolgemuth, 1972).

Seawater at all depths in the ocean appears to be undersaturated with respect to barium in equilibrium with pure barite by a factor of two or more (Church, 1979). Barium in deep-sea sediment pore waters is at saturation. Chow and Goldberg (1960) measured dissolved barium concentrations approaching saturation in water from 4,185 m in the Pacific Ocean. As would be expected, particulate barite, formed biologically (see discussion below) in the upper water column, begins to dissolve as it sinks slowly to the deep ocean floor, increasing the concentration of dissolved barium at depth (Dehairs *et al.*, 1980, 1987; Bishop, 1988; Lea and Boyle, 1989; Stroobants *et al.*, 1991). However, substantial amounts of particulate barium (barite) settle to and accumulate in deep-sea sediments.

Marine barites may actually be present as non-ideal solid solutions with strontium, $(\text{Ba,Sr})\text{SO}_2$, lowering saturated barium molalities and rendering surface waters nearly saturated with respect to barium (Church, 1979; Felmy *et al.*, 1993). Natural marine barites contain 0.3 to 3.0 percent strontium and 0.01 to 0.10 percent calcium (Church, 1979).

Other explanations of the apparent undersaturation of surface waters of the ocean with respect to barium are adsorption of Ba^{+2} to clay particles (Chan and Hanor, 1982), precipitation of barium as barite in decaying organic detritus (microbial degradation of detritus results in release of SO_4^{-2}) in the upper water column (Dehairs *et al.*, 1980, 1987; Stroobants *et al.*, 1991), and intracellular barite formation in marine plankton (Gooday and Nott, 1982; Fisher *et al.*, 1991; Lea and Boyle, 1991). Several species of marine and freshwater bacteria, protozoans, and phytoplankton are able to bioaccumulate dissolved barium from the ambient medium and precipitate it as barite in intracellular vacuoles.

Concentrations of dissolved barium in offshore surface waters of the world's oceans range from about 3 to about 34 $\mu\text{g/L}$ (30 to 170 nM/kg) (Table 3-3). There

does not seem to be any systematic trend from one ocean to another, with the

Table 3-3. Concentrations of dissolved barium in offshore surface waters of the oceans. All concentrations are in $\mu\text{g/L}$.

Water Body	Concentration	Reference
Oceanic average	15.0	Li, 1991
NE Atlantic	7.4-14.0	Rhein <i>et al.</i> , 1987
English Channel	6.2	Bowen, 1956
W Atlantic	5.6	Chan <i>et al.</i> , 1977
N Atlantic	2.6	Anderson and Home, 1968
N Atlantic	8.4	Wolgemuth & Broecker, 1970
S Atlantic	4.9	Bishop, 1990
Pacific	12.0	Chow & Goldberg, 1960
Pacific	8.5-10.7	Wolgemuth & Broecker, 1970
NW Pacific	11.0-12.0	Chow, 1976
NW Pacific	5.0	Chow & Snyder, 1980
NW Pacific	5.4	Roe and Froelich, 1984
Gulf of Alaska	4.2-19.4	Epstein & Zander, 1979
Gulf of Mexico	11.0-12.0	Chan & Hanor, 1982
Caribbean Sea	6.0-19.0	Falkner <i>et al.</i> , 1993
Arctic	6.04-6.7	Chan <i>et al.</i> , 1977
Black Sea	19.1-33.4	Falkner <i>et al.</i> , 1991, 1993
W. Mediterranean	11.0	Bernat <i>et al.</i> , 1972
Indian Ocean	10.3-12.9	Dehairs <i>et al.</i> , 1989

exception of the higher concentrations of barium in surface waters of the Black Sea than in other seas. Barium and radium concentrations in surface waters of the Black Sea have dropped in recent years, probably because of decreased vertical mixing in the water column due to eutrophication (Falkner *et al.*, 1991).

Concentrations of dissolved barium increase with depth in the ocean (Chow and Goldberg, 1960; Chow, 1976; Church, 1979; Falkner *et al.*, 1993). This may be caused in part by dissolution of particulate barite at depth. At a location in the

Black Sea sampled by Falkner *et al.*, (1993), the concentration of dissolved barium increased from 26.1 $\mu\text{g/L}$ at a depth of 10 m to 70.6 $\mu\text{g/L}$ at a depth of 115 m. In the San Diego Trough off Southern California, the concentration of dissolved barium in the water column in 1975 increased from 11 $\mu\text{g/L}$ at 1 m water depth to 22 $\mu\text{g/L}$ at a depth of 968 m (Chow, 1976).

Concentrations of barium in pore waters of deep-sea sediments usually are at saturation. Sediments near deep-sea hydrothermal vents may contain several thousand parts per million barium, caused by precipitation of barite in the presence of high concentrations of sulfate produced from the oxidation of sulfide released from the hydrothermal fluids (Varnavas, 1987; Shikazono, 1994). Up to 30 percent of the dissolved barium in deep ocean waters may be derived from submarine hydrothermal activity (Edmond *et al.*, 1979; Van Damm *et al.*, 1985).

Concentrations of particulate barium (much of it barite) in the ocean are much lower than those of dissolved barium. Trefry *et al.*, (1981) reported concentrations of 0.002 to 0.020 $\mu\text{g/L}$ of particulate barium in outer continental shelf waters of the Gulf of Mexico. Dehairs *et al.*, (1980) reported a mean of about 0.0205 $\mu\text{g/L}$ for particulate barium in the offshore Atlantic and Pacific. This may be caused in part by dissolution of particulate barite at depth. Slightly higher concentrations of particulate barite are present in surface waters of the Mediterranean Sea (0.014 to 0.168 $\mu\text{g/L}$) (Dehairs *et al.*, 1987). The concentrations of barium in the particles themselves range from about 400 to 5,000 mg/kg particles. Thus, dissolved barium accounts for more than 99 percent of the total barium in surface waters of the ocean.

Concentrations of particulate barium decrease with increasing depth, suggesting gradual dissolution during sinking. Some of the barite forms in surface waters in aggregates of decaying organic matter (detritus) greater than about 50 μm in

average diameter (Bishop, 1990). The size of barite particles decreases with increasing depth in the ocean. In deeper waters below 100 to 200 m, most barite particles are about 1 μm in diameter and show evidence of surface etching from dissolution (Dehairs *et al.*, 1980).

RIVERINE INPUT OF BARIUM

Rivers of the world contribute substantial amounts of barium to the ocean. Several examples have been reported of higher concentrations of dissolved barium in the oligohaline portions of river estuaries than in the upstream and oceanic portions of the river (Hanor and Chan, 1977; Edmond *et al.*, 1978; Li and Chan, 1979; Moore and Edmond, 1984; Xiangfei *et al.*, 1990). American rivers contain from 9 to about 152 $\mu\text{g/L}$ dissolved barium (Durum and Haffty, 1961). Chan and Hanor (1977) reported an average of 61.7 $\mu\text{g/L}$ dissolved barium in the Mississippi River over a 17-hour period. These concentrations are well below the saturation concentration of barite barium in fresh water (1,360 $\mu\text{g/L}$: Burton *et al.*, 1968). Barium readily adsorbs to suspended clay, iron oxide, and organic particles (Grim, 1968; Lagas *et al.*, 1984), possibly explaining the low concentration of dissolved barium in river water which usually has a high concentration of suspended clay-sized particles.

The average concentration of barium in suspended particles in rivers is about 600 mg/kg (Martin and Meybeck, 1979). Trefery *et al.*, (1981) reported a concentration of 740 mg/kg barium in Mississippi River suspended particles. Some of the barium associated with suspended clay particles is adsorbed by ionic exchange to the clay particle surfaces and is readily exchanged for other ions as the ionic concentration of the water increases in the estuarine portions of a river estuary (Hanor and Chan, 1977). Approximately 7.4 percent of the particulate barium in the Zhujiang River estuary is in an exchangeable form (Xiangfei *et al.*, 1990).

In the Mississippi River, dissolved barium concentrations increase from an average of about 64 $\mu\text{g/L}$ in the freshwater portion of the river to as high as 80 $\mu\text{g/L}$ in the oligohaline portions (0 to 9 ‰ salinity) of the estuary (Hanor and Chan, 1977). Concentrations of dissolved barium then decrease with increasing salinity in the lower estuary, eventually reaching the concentration in the open Gulf of Mexico ($\approx 11 \mu\text{g/L}$). The increase in dissolved barium in the oligohaline regions of the estuary is caused by the release of sorbed barium from clay particles through ion exchange. These ion exchange reactions occur very rapidly for barium (Li *et al.*, 1984). Most of the barium desorbing from suspended sediments in the oligohaline region of the Zhujiang Estuary, China, is from the readily-exchangeable fraction on the clay particles (Xiangfei *et al.*, 1990). In the Zaire River (Congo), dissolved barium concentrations increase only slightly from 19.7 $\mu\text{g/L}$ in fresh water to about 22 $\mu\text{g/L}$ at a salinity of 2.08 ‰ (Edmond *et al.*, 1978). Dissolved barium concentrations then decrease to about 7.2 $\mu\text{g/L}$ at the mouth of the estuary. In the Hudson River, the concentration of dissolved barium increases from 30.3 $\mu\text{g/L}$ in the freshwater portion of the river to 36.5 $\mu\text{g/L}$ at a salinity of 3 ‰, and then decreases to values typical of the New York Bight (7.6 to 9.3 $\mu\text{g/L}$) (Li and Chan, 1979). Suspended particulate matter in the Hudson River contains 680 mg/kg barium (Li *et al.*, 1984). The distribution coefficient (ratio of barium concentration on particles to barium concentration in the water) decreases by nearly two orders of magnitude between the freshwater and low-salinity (0 to 10 ‰) regions of the Hudson River estuary, indicating substantial desorption of barium from the suspended particles into the water.

Trefry (1982) estimated that rivers contribute a total of 1.3×10^{13} g (13 million metric tons) of barium to the oceans of the world each year. About 85 percent of the total barium discharged by rivers is associated with suspended particles. The remainder is in solution.

A similar estimate can be produced for the Mississippi River alone, so that a comparison can be made with barium discharges to the Gulf of Mexico in produced water. The Mississippi River has a water discharge of approximately 580 km³/year (580x10¹² L/y) ; the total discharge contains an average of 210x10⁶ metric tons of suspended particulate matter (Milliman, 1990). If it is assumed that Mississippi River water contains an average of 60 µg/L (6x10⁻¹¹ metric tons/L) barium in solution (Chan and Hanor, 1977) and 740 mg/kg (740 g/metric ton) barium associated with suspended particles (Trefry *et al.*, 1981), the following particulate and dissolved fluxes of barium occur:

Mississippi River particulate Ba flux:

$$(210 \times 10^6 \text{ tons of particles/y}) \times (740 \text{ g Ba/ton}) = 155,400 \text{ tons/y}$$

Mississippi River dissolved Ba flux:

$$(580 \times 10^{12} \text{ liters of water/y}) \times (6 \times 10^{-11} \text{ tons Ba/L}) = 34,800 \text{ tons/y}$$

The total annual input of barium to the Gulf of Mexico from the Mississippi River is 190,200 tons/year, 82 percent of which is associated with suspended particles.

An estimated total of 547x10⁶ L/d (199.7x10⁹ L/y) of produced water is discharged to the northwestern Gulf of Mexico (Boesch and Rabalais, 1989a). If it is assumed that the average concentration of barium in the produced water is 50,000 µg/L (5x10⁻⁸ metric tons/L) (Macpherson, 1989; Neff *et al.*, 1989c), the following amount of barium is discharged in produced water to the Gulf of Mexico each year:

$$(199.7 \times 10^9 \text{ liters of produced water/y}) \times (5 \times 10^{-8} \text{ tons Ba/L}) = 9,985 \text{ tons/y}$$

The estimated discharge of barium in produced water is approximately 5 percent of the total amount discharged each year by the Mississippi River, but about 29 percent of the dissolved barium discharged by the Mississippi River each year.

Chan and Hanor (1982) reported elevated concentrations of dissolved barium (31 to 67 $\mu\text{g/L}$) in Gulf of Mexico waters south of Barataria Bay, LA, about 40 km west of the main pass of the Mississippi River, an area of intensive offshore oil and gas production. Although they suggested that some of this excess dissolved barium (compared to a background concentration of 10-11 $\mu\text{g Ba/L}$ in the open Gulf) could have come from discharges from offshore platforms, they were able to account for most of the excess as a result of the non-conservative mixing of Mississippi River water with Gulf of Mexico water (Figure 3-2). As described above, barium was desorbing from suspended particles upon mixing of river water with sea water, producing higher concentrations of dissolved barium in waters of the mixing zone than occurred in either the river itself or in offshore waters of the Gulf. As the Mississippi River plume mixes with waters of the open Gulf of Mexico, its salinity increases and dissolved barium concentrations decrease as barium is diluted, precipitates as barite, or resorbs to suspended particles.

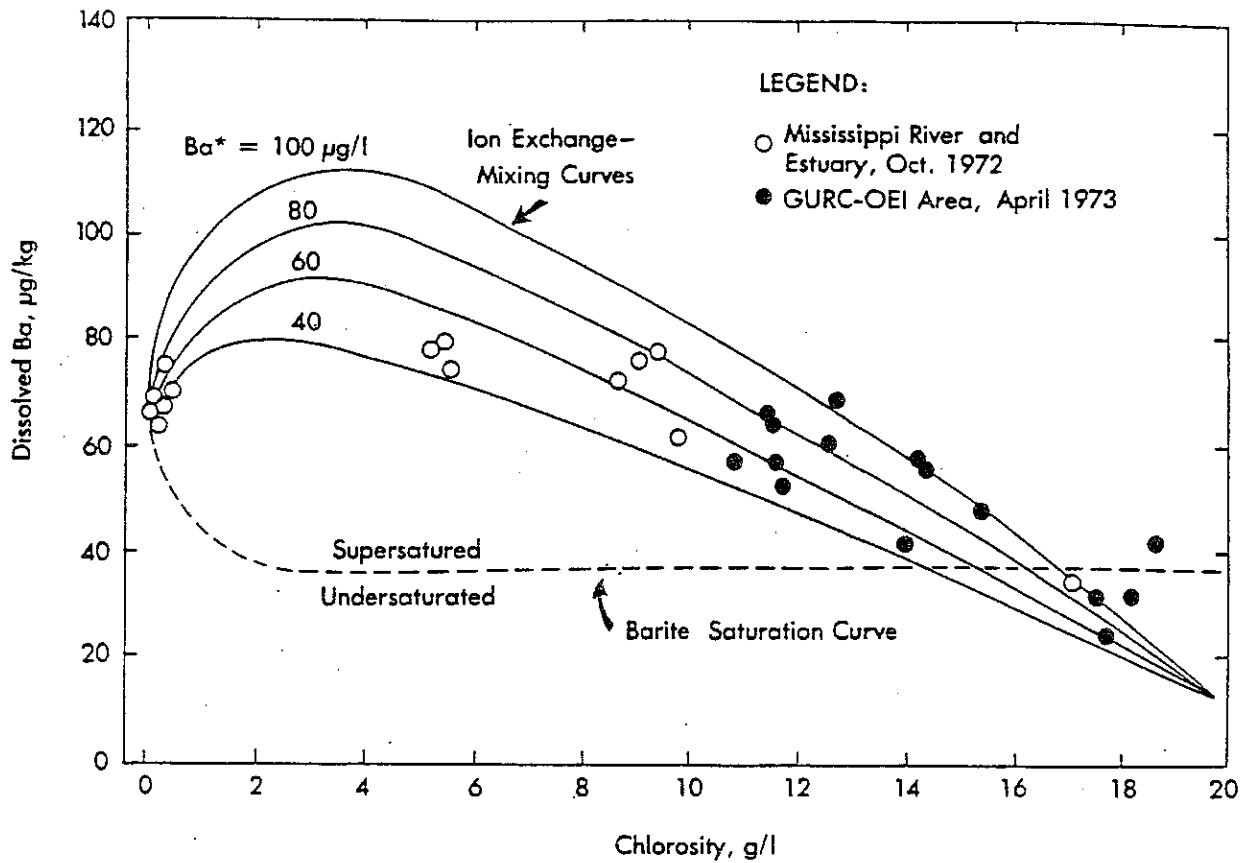


Figure 3-2. Variation in dissolved barium concentrations as a function of chlorosity (concentration of total inorganic halides other than fluoride per liter of seawater at a given temperature for waters of the Mississippi River estuary, October, 1972 (open circles) and Louisiana coastal waters, April, 1973 (solid circles). Solid lines are calculated ion exchange curves for concentrations of adsorbed barium. The dashed line is the theoretical barite saturation curve. From Chan and Hanor (1982).

Section 4

PRECIPITATION OF BARIUM DURING MIXING OF PRODUCED WATER AND SEA WATER

ACTIVITY OF BARIUM AND SULFATE IN PRODUCED WATER AND SEA WATER

Because produced water often contains high concentrations of barium in apparent solution and sea water contains high concentrations of dissolved sulfate (about 28 mM), it is expected that when produced water is discharged to and mixed with the ocean, barium will precipitate as barite. However, no measurements have been made of the rate of precipitation of barium in the receiving waters of a produced water discharge. Neff *et al.*, (1989c) reported uniformly high concentrations of barium (about 2,000 mg/kg) in sediments in Terrebone Bay, LA, where produced water had been discharged from many oil-water separators for nearly half a century. Similarly, Boothe and Presley (1985) reported elevated concentrations of barium in surficial sediments around several production platforms in the western Gulf of Mexico. Background concentrations of barium in sediments of the northwestern Gulf of Mexico are in the range of 200 to 800 mg/kg (Boothe and Presley, 1985). Most of the excess barium in sediments near production platforms probably is derived from water-base drilling fluids (containing high concentrations of barite weighting agent) which were discharged from the platforms to the ocean during well drilling. However, some of the barium in the sediments may have come from precipitation of barium from produced water following its discharge to the ocean.

To precipitate as barite, molal concentrations of barium and sulfate must exceed the solubility product for barite ($\approx 1.05 \times 10^{-10}$ @ 25°C). This criterion is easily met considering the high concentrations of sulfate in seawater and of barium in many produced waters.

Sulfate ion is one of the more abundant anions in seawater. A typical concentration of sulfate in sea water from the open Gulf of Mexico off the Mississippi River (Hanor and Chan, 1977) is 2,760,000 $\mu\text{g/L}$ (0.029 M). In open ocean water, there is a nearly constant relationship between sulfate concentration and chlorinity (the concentration of total halides other than fluoride per kg sea water): $\text{SO}_4^{2-}/\text{Cl} = 0.1400$. In coastal waters and estuaries influenced by freshwater runoff, this relationship is more variable; estuarine waters often have lower relative concentrations of sulfate because of the low concentration of sulfate in many river waters.

Not all the sulfate in sea water is in the free ionic form; some is complexed with various cations. In a complex ionic medium such as sea water, approximately 39 percent ($f = 0.39$) of the total sulfate is in a free, undissociated form (Church and Wolgemuth, 1972). The remainder is complexed, mainly with sodium and magnesium (Hanor, 1969). Church and Wolgemuth (1972) estimated that the single ion activity coefficient, γ , of sulfate in seawater at 25°C and 1 atm is 0.17. Thus, the apparent activity coefficient of ionic sulfate in seawater, Γ , is equal to $\gamma_i f_i$, 0.066. Because the activity of an ion in solution is a function of the ionic strength, ionic composition, temperature, and pressure of the solution, the activity of free, ionic sulfate may change during mixing of produced water and sea water.

According to Hanor (1969), more than 93 percent of the barium in sea water is in the free ionic form. Most of the complexed barium is complexed with sulfate. The single ion activity coefficient for barium in seawater is approximately 0.24, giving an apparent activity coefficient, Γ , of 0.22 (Church and Wolgemuth, 1972). The apparent free ion activity of barium in produced water is not known. Very little of the barium in produced water is filterable (particulate). Because the sulfate concentration of produced water usually is much lower than that of sea water, it is probable that very little of the barium in produced water is complexed with sulfate. Some of the barium may be complexed with chloride and bicarbonate (HCO_3^-)

which sometimes are present at high concentrations in produced water (Kharaka *et al.*, 1978; Sturchio *et al.*, 1993).

Some of the barium in produced water also may be complexed with low molecular weight organic acids that may be present at concentrations of several thousand parts per million (Table 3-2). The organic acids in produced water include a homologous series of aliphatic acids from acetic to at least decanoic acid, dicarboxylic acids, such as succinic acid, aromatic acids, such as benzoic acid, and cyclic acids, such as cyclohexane carboxylic acid (Somerville *et al.*, 1987; Barth, 1991; Means and Hubbard, 1987; McGowan and Surdam, 1988).

Drummond and Palmer (1986) estimated that, at the pH of most formation waters (6-8), most of the acetate would be present as the acetate anion. They also predicted that, under hot, geopressured conditions in the formation, formation constants for metal-acetate complexes would be much higher than for the analogous metal-chloride complexes, favoring metal-acetate complexes even in high-salinity brines.

Shock and Koretsky (1993) came to different conclusions. They predicted the speciation of acetate, alkaline earth elements, and sulfur in a produced water typical of east Texas production wells. The produced water modeled had a brine concentration (NaCl) of 1.0 molal (58.4 ‰ salinity) and contained 500 ppm calcium, 20 ppm strontium, 10 ppm barium, 2 ppm sulfur, and 400 ppm acetate. Their model predicted that most of the acetate was present as the free anion, with about 38 percent complexed with sodium and calcium. Only 2.24 percent of the barium was predicted to have complexed with acetate (Table 4-1). By comparison, 2.18 percent of the calcium, 1.73 percent of the strontium, and 1.43 percent of the magnesium was predicted to have complexed with acetate. The sulfur was predicted to have been present primarily as dissolved H₂S (73 percent) and sulfide ion (27 percent). The authors concluded that acetate complexes are ineffectual in

Table 4-1. Predicted speciation of acetate, sulfate, and alkaline earth elements in a typical saline (1.0 M NaCl) produced water at 125°C. From Shock and Koretsky (1993).

Chemical/Species	Percent	Chemical/Species	Percent
Acetate		Barium	
CH ₃ COO ⁻	55.07	Ba ⁺²	78.24
NaAc	34.00	BaCl ⁺	19.44
CH ₃ COOH	6.33	BaAc ⁺	2.24
CaAc ⁻	4.01		
Strontium		Calcium	
Sr ⁺²	71.83	Ca ⁺²	84.12
SrCl ⁺	26.36	CaCl ⁺	8.07
SrAc ⁺	1.73	CaHCO ₃ ⁺	3.25
		CaCl ₂	2.32
		CaAc ⁺	2.18
Magnesium		Sulfur	
Mg ⁺²	66.19	H ₂ S (aqu.)	72.76
MgCl ⁺	30.90	HS ⁻	27.24
MgHCO ₃ ⁺	1.45		
MgAc ⁺	1.43		

transporting major rock forming elements or trace metals in sedimentary basin brines. They suggested that acetate complexes may be more important in low-salinity waters containing high concentrations of organic matter.

Just as oxalate (a dicarboxylic acid) is more efficient than acetate (a monocarboxylic acid) in complexing and solubilizing trivalent aluminum ions (Surdam *et al.*, 1984; McGowan and Surdam, 1988), dicarboxylic acid anions may be more efficient than monocarboxylic acids in complexing divalent barium ions. Eleven samples of produced water from the onshore Santa Maria Basin contained 724,000 to 7,160,000 µg/L total organic acids, including 27,000 to 1,560,000 µg/L (1.9 to 32.5 percent) dicarboxylic acids (McGowan and Surdam, 1988). Produced water from an on-shore facility at Carpinteria, California, contained

13,000 $\mu\text{g/L}$ barium and 21,000 $\mu\text{g/L}$ sulfur (Higashi *et al.*, 1992). Another produced water sample from the same area analyzed by the same group of investigators (Fan *et al.*, 1992) contained 70,000 $\mu\text{g/L}$ barium and 10,000 $\mu\text{g/L}$ sulfate. If produced waters from the Carpinteria area examined by Hibashi *et al.*, (1992) and Fan *et al.*, (1992) are comparable to those from the onshore Santa Maria basin examined by McGowan and Surdam (1988), the up to one-hundred-fold excess of dicarboxylic acid anions over barium cations may be sufficiently high that most of the barium in the produced water is carried in solution as barium-dicarboxylic acid complexes.

The high sulfur concentration in the Carpinteria samples also suggests that some of the barium could be present in the produced water as a $\text{Ba}^{+2}\text{-S}^{-2}$ complex, because most of the inorganic sulfur in produced water under the reducing conditions of the produced water reservoir is expected to be in the form of sulfides (Table 4-1).

Desai *et al.*, (1969) reported that natural dissolved organic matter at concentrations of a few thousand $\mu\text{g/L}$ increased the apparent solubility of barium in sea water. This apparent solubilization of barium could have been caused by complexation of barium with the dissolved organic matter. Lagas *et al.*, (1984) reported that barium was leached readily from soil columns, mainly in the form of organic (mainly fatty acid) Ba-complexes.

If barium in produced water has an apparent free ion activity coefficient similar to that in sea water ($\Gamma = 0.22$), then only a small fraction of the barium from produced water can remain in solution in the saline receiving waters of a produced water discharge, assuming equilibrium. However, if a significant fraction of the barium in produced waters containing high concentrations of organic acid anions is complexed with the organic acids, the activity of barium in the produced water would be greatly reduced and barite precipitation would be slowed.

BEHAVIOR OF BARIUM DURING MIXING OF PRODUCED WATER WITH SEA WATER

Granbakken *et al.*, (1991) and Haarberg *et al.*, (1992) modeled the behavior of alkaline earth elements in produced water during mixing of produced water with seawater following injection of seawater into a petroleum-bearing formation. The solubility of barite increases with increasing temperature, pressure, and ionic strength (Haarberg *et al.*, 1992). The rate of barite precipitation increases with increasing specific surface area of seed crystals (Granbakken *et al.*, 1991). The model predicts that, when nine parts produced water containing 50,000 $\mu\text{g/L}$ barium are mixed with one part sea water (90% produced water/10% seawater) containing 3,077,000 $\mu\text{g/L}$ sulfate, more than 90 percent of the equilibrium concentration of barite is precipitated within about six minutes at a temperature of 91.4°C and a pressure of 312 bar.

Rolheim *et al.*, (1993) studied the kinetics of BaSO_4 and SrSO_4 scale formation in steel tubing under conditions simulating production of oil and produced water from a well. Two water streams, one containing dissolved barium (as $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$) and the other containing sulfate as (Na_2SO_4), were mixed in a dynamic mixing chamber to produce a solution containing 0.4 mM ($\approx 56,000 \mu\text{g/L}$) barium and 4.0 to 6.4 mM ($\approx 384,000$ to $614,000 \mu\text{g/L}$) sulfate and pumped immediately at different rates through steel pipes of different diameters. Concentrations of barium in the water and barite on the walls of the pipe were measured periodically at different distances to 16 m from the mixing point.

The concentration of dissolved barium in the water decreased from 56,000 $\mu\text{g/L}$ to 49,000 $\mu\text{g/L}$ in the first 0.14 m of pipe, probably due to nucleation of barite crystals in the water phase. Barium concentration then decreased more gradually to about 18,000 $\mu\text{g/L}$ at 16 m from the point of initial mixing. The barium concentration after initial mixing was estimated to be about 26 times the saturation concentration in equilibrium with solid barite.

The rate of barite precipitation was much higher in pipe that contained a layer of barite scale, indicating that surface area for nucleation was an important determinant of precipitation rate. In clean pipe, 15 to 40 percent of the barite formed remained in suspension as particles in the flowing water. More than 95 percent of the barite that precipitated in pipe that was already coated with scale precipitated on the scale.

These studies show that barite may precipitate quickly (seconds to minutes) from mixtures of water containing high (several times saturation) dissolved barium and sulfate concentrations, particularly if nuclei are present. Christy and Putnis (1993) showed that when concentrations of dissolved Ba^{+2} plus SO_4^{-2} in low-salinity water exceed the solubility product by eight-fold or more with respect to barite, rapid homogeneous nucleation of amorphous barite takes place in the water phase. At lower levels of supersaturation, precipitation is slower and occurs preferentially on barite crystal surfaces. In the presence of 1 molal NaCl, precipitation is irregular, probably due to variable amounts of barite particles in suspension in the reaction mixture. At barium and sulfate concentrations 2.5 to 8.0 times saturation, precipitation of barite onto the surface of preexisting barite crystals follows a second-order rate law. The activation energy for precipitation of 22.0 kJ/mol, estimated by Christy and Putnis (1993), is similar to the activation energy of 33.5 kJ/mol estimated for barium precipitation at 25 to 125°C in a saline medium used by Granbakken *et al.*, (1991) in their model.

At low degrees of supersaturation (less than a saturation index [S] of about 20, defined as the ratio $[m_{\text{Ba}^{+2}}][m_{\text{SO}_4^{-2}}]/K_{sp}$, where K_{sp} is the molal solubility product at equilibrium), the rate of barite precipitation is controlled by a surface reaction mechanism (polynuclear growth); at higher degrees of supersaturation, the rate of barite precipitation is controlled by a bulk diffusion mechanism (Symeopoulos and Koutsoukos, 1993; Shikazono, 1994). Bulk diffusion is facilitated by mixing, so barite precipitation from a well-mixed, highly supersaturated solution is rapid.

Symeopoulos and Koutsoukos (1993) showed that, when [^{131}Ba] barium nitrate was mixed rapidly with a standard solution of sulfuric acid so that the mixture contained equimolar concentrations of Ba^{+2} and SO_4^{-2} , the time to induction of precipitation and precipitation rate were related to the degree of supersaturation of the mixture with respect to Ba^{+2} and SO_4^{-2} . Time to induction of precipitation decreased from 33 minutes at $S = 8.67$ to 3 minutes at $S = 16.66$. The rate of precipitation increased 100-fold as S increased from 8.67 to 16.6.

Because the conditions of the experiments performed by Christy and Putnis (1993), Symeopoulos and Koutsoukos (1993), and Shikazono (1994) do not exactly simulate the physical chemical and mixing conditions of produced water with sea water in the ocean, it is not possible to estimate the rate of precipitation of barite in the receiving waters of a produced water discharge using these rate data and activation energies. However, these empirical and modeled results do indicate that barite precipitation does occur rapidly in aqueous solutions that are at least eight-fold supersaturated with respect to active dissolved species of barium and sulfate, and that precipitation rate increases with increasing supersaturation and increasing surface area of suitable crystal nuclei.

Concentrations of particulate barium in Gulf of Mexico produced water appear to be very low, despite high concentrations of dissolved barium (Boesch and Rabalais, 1989b; Neff *et al.*, 1989c). Filtration (0.45- μm filter) did not remove quantifiable amounts of barium. However, small amounts of sub-micron particles may have been present; these would catalyze precipitation. The results of Rolheim *et al.*, (1993) and Christy and Putnis (1993) indicate that nuclei are not required to initiate precipitation of barite if the solution is sufficiently supersaturated with dissolved barium and sulfate. Once precipitation is initiated, the newly-formed barite particles serve as nuclei for accelerated precipitation.

Barium probably precipitates rapidly (minutes) from produced water containing low concentrations of organic acids and more than about 500 $\mu\text{g/L}$ free, ionic barium, even in the absence of barite nuclei. The saturation concentration of dissolved, active Ba^{+2} in a 50:50 mixture of produced water and sea water is about 100 $\mu\text{g/L}$, assuming that the sulfate concentration in the mixture is about one-half (0.014 M) that of full-strength sea water and that the activity coefficients of divalent ions in the mixture are about 0.1 (Chow and Goldberg, 1960). Many surfaces, not just the surface of barite crystals, can serve as nucleation centers for initial precipitation of barite. Suspended inorganic and organic particulate matter in natural seawater, and even irregularities in the inner surface of pipes in the produced water treatment and discharge system, can serve as nucleation centers for initiation of crystal growth. As barium concentration in the produced water/seawater mixture increases above the equilibrium concentration, the rate of precipitation increases.

As an example, a typical Gulf of Mexico produced water contains about 50,000 $\mu\text{g/L}$ (0.364 M) dissolved barium; Gulf of Mexico sea water contains about 0.029 M sulfate. Assuming an apparent activity coefficient of 0.2 for barium in produced water and an apparent activity coefficient of 0.17 for sulfate in sea water, a 50:50 mixture of Gulf produced water and Gulf sea water is nearly 800X supersaturated with respect to BaSO_4 ; a 90:10 sea water:produced water mixture is about 300X supersaturated, and a 99:1 sea water:produced water mixture is about 30X supersaturated. The rate of precipitation of barite from such highly supersaturated mixtures is diffusion-rate limited (Shikazono, 1994), so precipitation is likely to be very rapid in a well-mixed receiving water environment.

If the free ion activity of Ba^{+2} in the produced water is lower than about 0.1 because of complexation of barium with organic acids or sulfide, precipitation may be delayed, but not inhibited completely. Because of the extremely low solubility product for barite ($\approx 1.05 \times 10^{-10}$) and the finite distribution coefficient between dissolved and complexed Ba^{+2} , barium will precipitate as barite, the rate being

determined by the extent to which the produced water/seawater mixture is supersaturated with respect to total barite and the fraction of the barium that is complexed.

If scale inhibitors are used to prevent scale formation in the production tubing or produced water treatment system, they probably will inhibit precipitation of barium during initial mixing of produced water in the sea. Phosphate esters, phosphonates, and acrylic acid polymers are used in the U.S as scale inhibitors (Hudgins, 1989, 1992). These compounds are water-soluble and are discharged to the ocean in the treated produced water. They inhibit crystal nucleation and growth. Although they are diluted rapidly to ineffective concentrations upon discharge of produced water to the ocean, scale inhibitors nevertheless may delay the initiation or rate of precipitate formation. Their toxicity to marine organisms is low (median lethal concentrations, 1,200,000 to >10,125,000 $\mu\text{g/L}$), so they do not contribute significantly to the toxicity of produced water (Hudgins, 1992).

Section 5 TOXICITY OF BARIUM

TOXICITY TO MARINE ORGANISMS

Particulate barite is essentially inert toxicologically to marine organisms; most bioassays with marine organisms have produced median lethal concentrations greater than 7,000,000 $\mu\text{g/L}$ suspended barite (National Research Council, 1983). Barium (as barite) was reported to be toxic to embryos of the crab *Cancer anthonyi* at concentrations greater than 1,000,000 $\mu\text{g/L}$ (Macdonald *et al.*, 1988). This concentration is 20,000 times higher than the aqueous solubility of barium in sea water, indicating that the observed effects due to particulate rather than soluble barium. Schatten *et al.*, (1985) reported that barite at concentrations greater than 1 mM (137,000 $\mu\text{g/L}$ barium) interfered with several processes associated with fertilization and early development of sea urchin eggs. This concentration is more than 2,700 times higher than the seawater solubility of barium. A 10 mM mixture of barite in sea water, if centrifuged to remove undissolved, particulate barite, was without significant effects on early development, indicating that effects were caused by barite particles, not Ba^{+2} ions in solution. The authors reported that barium, probably in the form of barite, was deposited on the outer surface of the eggs during exposure to the barite suspensions, contributing to the observed effects of high concentrations of suspended barite particles.

Swimming activity of larvae of dungeness crabs and dock shrimp was inhibited during exposure for 24 to 119 hours to suspensions of 16,200,000 to 71,400,000 $\mu\text{g/L}$ barite (Carls and Rice, 1984). The crustacean larvae recovered quickly when returned to particle-free sea water. Similar responses were produced with suspensions of bentonite clay, indicating that the responses were caused by physical or behavioral interactions with suspended particles, not to any toxic properties of suspended barite.

Long-term exposure to 500,000 $\mu\text{g/L}$ barite caused changes in calcium concentrations in various tissues and accumulation of barium in the hepatopancreas (probably as barite particles) and exoskeleton of grass shrimp *Palaemonetes pugio* (Brannon and Rao, 1979). Shrimp exposed to a substrate of particulate barite for up to 106 days ingested the barite particles (Conklin *et al.*, 1980). Barite particles in the gut caused lesions in the gut epithelium, probably by abrasion.

Barite mixed with or layered on top of marine sediments inhibited colonization and altered the benthic community structure of the sediments (Tagatz and Tobia, 1978; Cantelmo *et al.*, 1979; Starczak *et al.*, 1992). These effects were attributed to alterations of sediment texture by the dense, fine-grained barite, rendering the substrate unsuitable for some species and more suitable for other species settling as larvae from the plankton.

Few studies have been published dealing specifically with the toxicity to marine organisms of dissolved barium. Higashi *et al.*, (1992) fractionated produced water from a California production facility and determined the toxicity of the fractions to embryos of the mussel *Mytilus californianus* (Table 5-1). The unfractionated produced water (fraction I) was moderately toxic (EC_{50} 2.12 percent produced water: the concentration causing 50 percent decrease in shell deposition during exposure for 48 hours). The non-volatile fraction (II), generated by freeze-drying the produced water, was slightly less toxic (EC_{50} 2.86 percent), indicating that most of the toxicity of the produced water resided in the non-volatile fractions. Sequential solvent extraction of fraction II generated a nonpolar (III, containing hydrocarbons) and an intermediate polar (IV, containing several slightly polar organic compounds, such as phenols) fraction that were not toxic. The residue was dissolved in distilled water to produce a water-soluble fraction (V) containing inorganic cations and anions, as well as polar organic compounds. This water-soluble fraction was nearly as toxic (EC_{50} 2.65 percent) as the unfractionated

Table 5-1. Barium Concentrations ($\mu\text{g/L}$) and Toxicity (EC_{50} : Percent Produced Water Causing a 50 Percent Reduction in Shell Growth in Mussel Larvae) of Produced Water Fractions from Southern California. See Text for an Explanation of the Produced Water Fractions. From Higashi *et al.*, (1992).

Produced Water Fraction	Barium in Fraction	Toxicity (EC_{50})	Barium @ EC_{50}
I	13,000	2.12	275.6
II	--	2.86	--
III	--	≈ 15	--
IV	1,600	$>> 20$	$>> 320$
IVa	< 2.0	$>> 20$	$>> 0.4$
IVb	--	$>> 20$	--
V	18,000	2.65	477
VIa	12,000	2.87	344
VIb	--	4.63	--
VII	4.0	$>> 20$	$>> 0.8$
Sea Water	37	--	--

produced water (fraction I). The water-soluble fraction (V) was fractionated further by passing it through a Chelex ion-exchange resin to produce a fraction (VI) containing the polyvalent cations and a fraction (VII) containing polar organic compounds, anions, and monovalent cations. Fraction VII was not toxic. Material retained by the Chelex resin (VI) was eluted with 1N hydrochloric acid to produce fraction VIa which contained the cations and most of the toxicity of the original produced water (Table 5-1). Another fraction (VIb), possibly containing highly polar organic material, was eluted with acidic methanol and was about half as toxic as fraction VIa.

The produced water and its fractions were analyzed for a large number of metal and non-metal cations and anions commonly found in produced water. The only

cations, of those analyzed, that were present at higher than trace concentrations were barium and strontium. Therefore, Higashi *et al.*, (1992) attributed the toxicity of the produced water sample to barium and possibly strontium. The concentration of dissolved strontium is high in sea water (about 8,000 $\mu\text{g/L}$), comparable to its concentration in the produced water sample (13,000 $\mu\text{g/L}$) and its water-soluble extracts (7,500 to 10,000 $\mu\text{g/L}$). Therefore, it is unlikely that strontium contributed significantly to the toxicity of the produced water.

The concentration of barium in the produced water and water-soluble extracts containing most of the produced water toxicity (V and VIa) was in the range of 12,000 to 18,000 $\mu\text{g/L}$; the less toxic fractions contained 2 to 1,600 $\mu\text{g/L}$ barium (Table 5-1). Because inorganic anions (probably including any sulfate that may have been present in the produced water) were removed during fractionation, these concentrations may have been soluble in the distilled water solutions of the freeze-dried produced water sample (BaCl_2 has a solubility of about 310,000 $\mu\text{g/L}$ in distilled water).

At the EC_{50} concentrations of the produced water and its water-soluble extracts (2.12 to 2.87 percent of the original produced water, diluted and salinity-adjusted with concentrated seawater), the estimated concentrations of "dissolved" barium were 275 to 477 $\mu\text{g/L}$. These concentrations are seven to 13 times higher than the saturation concentration of barium in equilibrium with barite in sea water (using a saturation concentration of 37 $\mu\text{g/L}$). These concentrations also are about two orders of magnitude higher than barium concentrations necessary to cause acute toxic effects in freshwater organisms (discussed later).

It is probable that mixing the water-soluble fraction of the freeze-dried produced water with concentrated natural seawater to produce exposure media with the appropriate salinity for toxicity tests would result in the nearly immediate

precipitation of most of the barium in the freshwater extract, unless some of the barium was still complexed with organic acid anions. Thus, the mussel embryos

may have been responding to finely-particulate barite in suspension, barium-organic acid complexes, or to other cations in the seawater-extract mixtures.

Cherr and Fan (1993) reported that dissolved barium at concentrations of 300 and 400 $\mu\text{g/L}$ inhibited embryonic development, particularly cellular differentiation of the pre-gastrula stage of mussel (*Mytilus californianus*) embryos. Barium was introduced into exposure media as barium acetate, because it was the only form of barium that did not precipitate in sea water at concentrations of 10,000 $\mu\text{g/L}$ or less in 48 hours. This is consistent with the prediction that complexation with organic acids is likely to slow the rate of precipitation of barium in seawater. At exposure concentrations above 10,000 $\mu\text{g/L}$, where precipitation of barite was observed, the toxicity of the barium acetate to the mussel embryos decreased with increasing concentration, suggesting that it was barium ion or dissolved barium acetate that was causing toxic effects, not barite particles. Mussels deployed in cages at 1 and 10 m from the Carpinteria produced water outfall accumulated barium in their tissues to concentrations (0.7 and 1.04 mg/kg wet weight) higher than those in tissues of mussels deployed farther away (<0.48 mg/kg) (Cherr and Fan (1993).

The results of these studies suggest that dissolved or complexed barium at concentrations two or more times in excess of its saturation concentration, as barite, in seawater may be bioavailable and toxic to sensitive embryonic stages of marine organisms in laboratory toxicity tests. It is not yet certain whether barium (and possibly strontium) is responsible for the toxic responses observed in marine organisms near the produced water outfall from the Carpinteria produced water treatment facility (Osenberg *et al.*, 1992; Raimondi and Schmitt, 1992). Produced

water from onshore production wells in the general area of the Carpinteria facility is unusual in its high concentration of organic acids, particularly difunctional carboxylic acids which readily complex with divalent cations, such as barium (McGowan and Surdam, 1988). Thus, results of biological effects studies with produced water from the Santa Barbara Channel/Santa Maria Basin area should be extrapolated with caution to predict effects of discharges of produced water from other sources.

Four studies have reported effects on embryos of marine invertebrates of exposure to barium, either in solution, complexed with organic acids, or as suspended barite (Schatten *et al.*, 1985; Macdonald *et al.*, 1988; Higashi *et al.*, 1992; Cherr and Fan, 1993). These tests usually were performed in small containers with small volumes of water and high concentrations of embryos. It is possible that under these conditions, sufficient dissolved or complexed barium was present at the membrane surfaces of the embryos to compete with calcium and strontium (both abundant in sea water) for cellular biochemical reactions involving calcium cofactors (e.g., membrane permeability, microtubule function, and metamorphosis) (Tamm and Tamm, 1990; Ilan *et al.*, 1993). Effects of this type are much less likely in the receiving water environment where dispersion and dilution rapidly decrease concentrations of barite particles and dissolved/complexed barium and planktonic larvae are never exposed for extended periods of time to elevated concentrations of barium from produced water.

BIOACCUMULATION OF BARIUM BY MARINE ORGANISMS

Barite, barium, and metals associated with barite are not readily accumulated by marine animals even when the exposed species live in close association with high concentrations of barite or whole drilling muds in sediments. This represents an exposure regime that is extremely unlikely for organisms exposed to barium from produced water discharges. Under these conditions the barium is not passed

through marine chains (Neff, 1987; Neff et al. 1989a,b). When accumulated, the barium and other barite-associated metals often remain in the tissues as insoluble, inert concretions, probably of the original barite particles (Jenkins *et al.*, 1989).

Barium is bioaccumulated by marine organisms from natural concentrations in the ocean (Dehairs *et al.*, 1980, 1987; Fisher *et al.*, 1991; Stroobants *et al.*, 1991). Most marine plants and animals have tissue residues of a few mg/kg barium. Clams, *Maritrix maritrix*, from 12 coastal water sites along the Arabian Gulf, Saudi Arabia, contained mean barium concentrations in their soft tissues ranging from 0.28 to 3.98 mg/kg wet weight (Sadiq *et al.*, 1990). Muscle tissues of albacore tuna *Thunnus alalunga* caught off San Diego, CA, contained 0.005 to 0.007 mg/kg barium; other soft tissues contained 0.012 to 0.80 mg/kg barium and bones and teeth contained 0.95 to 1.9 mg/kg barium (Patterson and Settle, 1977). The average concentration of barium in soft tissues of marine organisms is 19 mg/kg (Li, 1991). A few species, such as marine planktonic xenophyophores, contain a few thousand mg/kg barium, mostly as intracellular barite crystals (Gooday and Nott, 1982). Barium also accumulates in the calcium carbonate skeletal tissues of marine plants and invertebrates (Bowen, 1956; Lea and Boyle, 1991). Skeletal tissues of stony corals are particularly rich in barium, with concentrations ranging from 8 to about 450 ppm, depending on species. Barium, although not a trace nutrient, is a natural constituent of the tissues of all living organisms.

TOXICITY TO FRESHWATER PLANTS AND ANIMALS

Freshwater plants and animals are not normally exposed to produced water discharges from offshore installations. The few published studies in the scientific literature indicate that dissolved barium is not very toxic to freshwater organisms. Some species of freshwater plants and protozoa actively accumulate dissolved barium from the water and deposit it in intracellular vacuoles as barite (Brook, 1980; Finlay *et al.*, 1983). The barium ions and barite crystals are not harmful to

the organisms and the dense barite may serve as a buoyancy control.

Jernelöv *et al.*, (1976) reported that dissolved barium at concentrations between 20,000 and 200,000 $\mu\text{g/L}$ caused a variety of sublethal effects in freshwater phytoplankton, invertebrates, and fish. Barium seemed to increase the toxicity of some metals to fish, possibly by complexing with and decreasing the activity of inorganic anions in the soft, fresh water, increasing the activity of the metal cations in solution.

Wang (1986) reported that dissolved barium at a concentration of 26,000 $\mu\text{g/L}$ in deionized water caused a 50 percent decrease in the growth rate of duckweed *Lemna minor*. Barium at concentrations up to 60,000 $\mu\text{g/L}$ in Illinois River water was completely nontoxic to duckweed. The author attributed the lack of toxicity of barium in river water to precipitation of barium as barite by reaction with sulfate (100,000 $\mu\text{g/L}$) in the river water. In subsequent experiments, Wang (1988) showed that the toxicity of barium to duckweed in natural fresh waters from different sources was inversely related to the sulfate concentrations in the natural waters. A concentration of 102,000 $\mu\text{g/L}$ barium was required to cause a 50 percent inhibition of growth in plants in the natural water sample with the highest sulfate concentration. Jenne *et al.*, (1980) showed that barite controls the concentration of barium in most fresh waters, including storm drainage, except soft, undersaturated waters, lending support to the conclusion of Wang (1986) that toxicity of barium in fresh water is controlled by sulfate concentration. Wang (1988) reported that the State of Illinois barium water quality standard for indigenous aquatic life is 5 $\mu\text{g/L}$.

TOXICITY TO HUMANS

The drinking water standard for barium in the United States is 1,000 $\mu\text{g/L}$ (Kojola *et al.*, 1978; Brenniman *et al.*, 1981). The federal standard for barium in effluents

destined for discharge to fresh waters is 100,000 $\mu\text{g/L}$ (Jackson *et al.*, 1990). The maximum acceptable human dose of barium in drinking water is 210 $\mu\text{g/kg/day}$ (EPA, 1992).

The basis for these standards was animal and human studies showing intense stimulation of smooth, striated, and cardiac muscle following ingestion of high doses of barium, leading to hypokalemia (low concentrations of potassium in the blood) and elevated blood pressure. However, epidemiological studies in which communities with drinking water containing an average of 7,300 $\mu\text{g/L}$ barium were compared with communities with drinking water containing an average of 100 $\mu\text{g/L}$ revealed that elevated concentrations of barium (seven times the national drinking water criterion) had no effect on the incidence or severity of high blood pressure (Brenniman *et al.*, 1981, 1984; Wones *et al.*, 1990). Thus, the threshold concentration of barium in drinking water that is toxic to humans is not known, but appears to be substantially higher than the national standards.

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