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# Metal Dispersion Resulting from Mining Activities in Coastal Environments: A Pathways Approach

BY RANDOLPH A. KOSKI



Stream impacted by acid rock drainage at the Beatson copper mine, Alaska. The water flows through sulfide-bearing waste piles before entering the ocean. The water has a pH of 5.3 and contains elevated concentrations of Fe, Cu, and Zn (Koski et al., 2008). The reddish precipitate is a mixture of ferrihydrite and schwertmannite that has adsorbed significant amounts of Cu and Pb.

**ABSTRACT.** Acid rock drainage (ARD) and disposal of tailings that result from mining activities impact coastal areas in many countries. The dispersion of metals from mine sites that are both proximal and distal to the shoreline can be examined using a pathways approach in which physical and chemical processes guide metal transport in the continuum from sources (sulfide minerals) to bioreceptors (marine biota). Large amounts of metals can be physically transported to the coastal environment by intentional or accidental release of sulfide-bearing mine tailings. Oxidation of sulfide minerals results in elevated dissolved metal concentrations in surface waters on land (producing ARD) and in pore waters of submarine tailings. Changes in pH, adsorption by insoluble secondary minerals (e.g., Fe oxyhydroxides), and precipitation of soluble salts (e.g., sulfates) affect dissolved metal fluxes. Evidence for bioaccumulation includes anomalous metal concentrations in bivalves and reef corals, and overlapping Pb isotope ratios for sulfides, shellfish, and seaweed in contaminated environments. Although bioavailability and potential toxicity are, to a large extent, functions of metal speciation, specific uptake pathways, such as adsorption from solution and ingestion of particles, also play important roles. Recent emphasis on broader ecological impacts has led to complementary methodologies involving laboratory toxicity tests and field studies of species richness and diversity.

## INTRODUCTION

Ore deposits are natural concentrations of metals or other elements that can be extracted from the earth for economic gain. For more than 5,000 years, mining has provided the raw materials that gave rise to the Bronze Age, the Roman Empire, and the Industrial Revolution. To maintain current living standards and to meet increasing global demands for mineral resources in the future, there will be continued pressure to open new mines. Although ore deposits occur in a variety of continental settings around the globe, many are located in coastal regions and on islands. Thus, mines of the future (like many of the past and present) will be located near coastal zones or what Cotté-Krief et al. (2000) refer to as the “globally critical land-ocean interface.”

Mining at any scale inevitably results

in a variety of raw and processed materials that must be moved, stored, and managed. These materials include low-grade waste rock and tailings—the pulverized, chemically treated fraction that remains after metals are extracted from ore. At some mines, the open-pit or underground workings, waste rocks, and tailings containment systems may be proximal to the shoreline. At others, rivers or constructed pipelines deliver tailings from concentrator facilities distant from the ocean to the coastal environment. Past mining practices have resulted in intentional and accidental disposal of mine wastes directly into bays, estuaries, and lagoons. The record of coastal contamination is long, extending back to the Copper and Bronze Ages (Davis et al., 2000). In recent years, disposal in waters farther offshore has become a preferred option for placement of mine

tailings (Ellis, 2008).

The mining and processing of ores to recover copper, lead, zinc, manganese, gold, silver, nickel, molybdenum, tin, phosphorus, uranium, iron, mercury, and other metals have had an impact on numerous coastal environments (Figure 1). In addition to potentially toxic ore metals, mineral deposits contain small but significant concentrations of other environmentally important trace elements such as arsenic, cadmium, and chromium. Under a range of climatic conditions, the physical and chemical breakdown of waste rocks and tailings (e.g., by erosion, weathering, and oxidation) initiates release of these elements and their transport into aquatic environments, with potentially severe consequences to local ecosystems.

Here, I describe the dispersal of metals along a series of pathways leading from source rocks to the marine biosphere. This approach is similar to the geoenvironmental modeling methodology developed by the US Geological Survey (Figure 2; Balistrieri et al., 2007) that links the mineralogical and chemical nature of the ores (source rocks), pathway processes that control transport and bioavailability of metals, and the uptake of metals by marine biota (bioreceptors). The emphasis here is on metal dispersion from base-metal sulfide deposits, that is, deposits mined for Cu, Pb, and Zn. The discussion of processes and pathways is based for the most part

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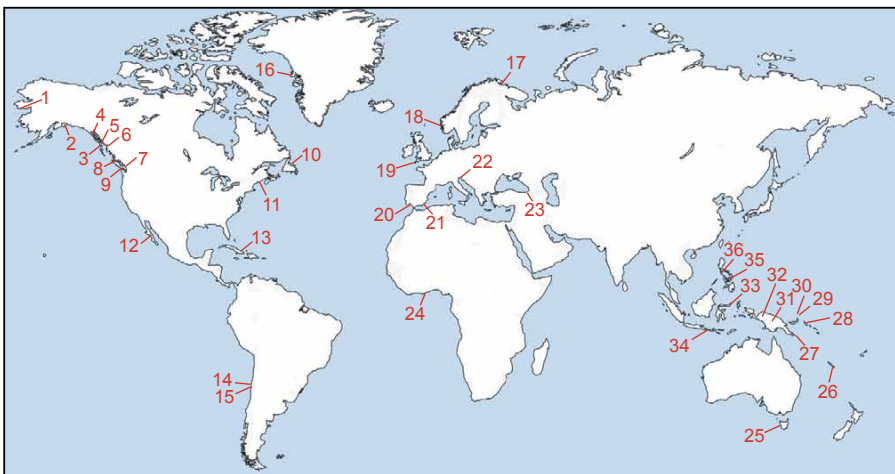
on well-studied sites in Spain (Gulf of Cádiz, Portman Bay), Chile (Chañaral Bay), the Philippines (Marinduque Island), and the United States (Callahan mine, Maine; Ellamar and Beatson mines, Prince William Sound, Alaska). Coastal zone water quality and ecological issues related to mining have received increasing international attention over the past three decades, resulting in a commensurate increase in research and publications. It is hoped that some of the lessons learned from environmental studies in shallow-water coastal environments will be useful in guiding

decision making for alternative methods of waste management, including deep-sea tailings disposal.

### NATURAL METAL FLUX: THE PRE-MINING BASELINE

In order to understand the true impact of mining-related contaminants, it is necessary to consider geochemical baselines—the natural variations in elemental concentrations in the surface environment prior to mining (Salminen and Tarvainen, 1997). All rocks and soils have a geochemical signature, and knowledge of baselines is essential to

remediation of contaminated sites. Some mineral deposits occur far inland from a coastal zone (e.g., El Salvador copper mine, Chile); thus, baselines for metal fluxes at the nearest shoreline may be equivalent to natural background levels. Other cases are more complicated. Contaminant baselines for rivers and estuaries downstream from modern mining activities in large mineralized areas such as the Iberian Pyrite Belt (IPB) in Spain may have been established by earlier mining practices. Baselines may also be difficult to establish for mineral deposits (e.g., Callahan and Ellamar mines in the United States) that were exposed at or below sea level prior to mine development. Climatic effects such as the deep weathering of mineralized rocks in tropical regions present additional complexity. Efforts to establish integrated geochemical baselines at the global scale are proceeding under sponsorship of the International Union of Geological Sciences (Plant et al., 2001; Reeder, 2007).



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|--|--|
| 1. Nome placer, USA (Au)                     | 19. St. Ives Bay, Hayle estuary, England (Sn)  |
| 2. Prince William Sound, USA (Cu)            | 20. Tinto and Odiel estuaries, Spain (Cu)      |
| 3. Bokan Mountain, USA (U)                   | 21. Portman Bay, Spain (Pb, Zn)                |
| 4. Klag Bay, USA (Au, Ag)                    | 22. Grado and Marano lagoons, Italy (Hg)       |
| 5. Salt Chuck mine, USA (Cu, Ag, Au)         | 23. Cayeli Bakir mine, Turkey (Cu, Zn)         |
| 6. Kitsault mine, Canada (Mo)                | 24. Gulf of Benin, Togo (P)                    |
| 7. Britannia mine, Canada (Cu, Zn)           | 25. Macquarie Harbor (estuary), Australia (Cu) |
| 8. Island Copper mine, Canada (Cu, Zn)       | 26. Southwest Lagoon, New Caledonia (Ni)       |
| 9. Jordan River mine, Canada (Cu)            | 27. Misima Island, Papua New Guinea (Au)       |
| 10. Little Bay, Tilt Cove mines, Canada (Cu) | 28. Bougainville Island, Papua New Guinea (Au) |
| 11. Callahan mine, USA (Zn, Cu)              | 29. Lihir Island, Papua New Guinea (Au)        |
| 12. Boleo, Lucifer mines, Mexico (Cu, Mn)    | 30. Simberi Island, Papua New Guinea (Au)      |
| 13. Levisa Bay, Cuba (Ni)                    | 31. Ok Tedi mine, Papua New Guinea (Cu, Au)    |
| 14. Ensenada Chapaco Bay, Chile (Fe)         | 32. Grasberg mine, Indonesia (Au, Cu)          |
| 15. Chañaral Bay, Chile (Cu)                 | 33. Buyat Bay, Indonesia (Au)                  |
| 16. Black Angel mine, Greenland (Zn, Pb)     | 34. Benete Bay, Indonesia (Cu, Au)             |
| 17. Sydvaranger mine, Norway (Fe)            | 35. Atlas mine, Philippines (Cu)               |
| 18. Sørørd, Norway (Cu, Pb, Zn)              | 36. Marinduque Island, Philippines (Cu)        |

Figure 1. Sites of mining and impacted coastal environments. Contamination from metals and other elements occurs in waters of estuaries, bays, deltas, and fjords. The principal ore metals are shown in parentheses.

### SOURCE ROCKS FOR METALS: SULFIDE MINERALS

In mining-impacted coastal zones, the main sources of environmentally sensitive metals are sulfide minerals exposed in (1) mine workings, waste rocks, and impounded tailings located onshore, and (2) tailings placed directly into the sea (Table 1). Iron sulfide minerals, either pyrite or pyrrhotite, are generally the dominant minerals by volume. Many deposits, for example in the IPB, are composed almost entirely of pyrite (Leistel et al., 1998). This abundance of Fe sulfides is important because they are the principal cause of ARD. The principal Cu source in the deposits is

chalcopyrite, whereas sphalerite and galena are primary sources of Zn and Pb, respectively. Although usually much less abundant, arsenopyrite is ubiquitous in sulfide deposits and a major source of As. The major sulfide minerals also contain minor to trace amounts of potentially toxic elements—for example, Ni, Co, and As in pyrite and Cd and Hg in sphalerite (Table 1). Ores typically are interlocking mixtures of sulfides and nonsulfide “gangue” minerals such as quartz (SiO<sub>2</sub>) and calcite (CaCO<sub>3</sub>). The nonsulfide minerals, especially carbonate minerals such as calcite, are important because they have the capacity to buffer acidity resulting from sulfide oxidation.

The relative amounts of individual sulfide minerals and the proportion of sulfide to nonsulfide mineral phases vary substantially among deposit types. At one end of the spectrum, porphyry-type copper deposits in Chile and the Philippines typically consist of disseminated grains and veins of sulfide dispersed in rocks composed of silicate minerals. Large tonnages of relatively low-grade (< 1 % total metals) ores are mined and milled. Conversely, massive sulfide deposits, such as the Callahan Cu-Zn mine in Maine, contain dense concentrations of sulfide that comprise more than 50% of the rock. In this latter case, the tonnages of rock mined are less, but the amounts of metal per unit volume of rock are much higher. Regardless of deposit type, waste rocks and tailings may contain large amounts of Fe sulfide minerals that are not of economic interest, but are nevertheless major contributors to ARD.

Mining and milling operations also affect the metal fluxes. Open-pit and underground mining methods expose

sulfide-bearing rocks to the atmosphere and surface water, and the exposure continues, in most cases, long after closure of the mine. Similarly, large volumes of sulfide-bearing rock debris with concentrations of metals below ore grade must be removed and piled on waste dumps adjacent to the mine. Mine tailings present still greater environmental challenges. Because the metal recovery process is not totally efficient, a fraction of the ore minerals as well as uneconomic pyrite, pyrrhotite, and arsenopyrite pass through the concentrator and are pumped in slurry form into containment facilities usually located at the surface near the mine site. The particle size for tailings is generally similar to fine sand or silt, and thus the chemically reactive surface area of sulfide minerals is greatly

increased. In addition, mine tailings contain chemical reagents added during processing of the ores (for example, xanthates, organic compounds used in froth flotation) that remain in the tailings during storage.

### PHYSICAL DISPERSION OF SULFIDE PARTICLES INTO THE OCEAN

The physical dispersion of sulfide minerals into marine settings occurs by mass wasting of mine debris into fluvial and estuarine systems, catastrophic release of tailings, and direct disposal of tailings offshore. In some cases, transport distances are minimal where mines have been constructed in and near the intertidal zone (Figure 3). In other cases, detrital sulfides in rivers can

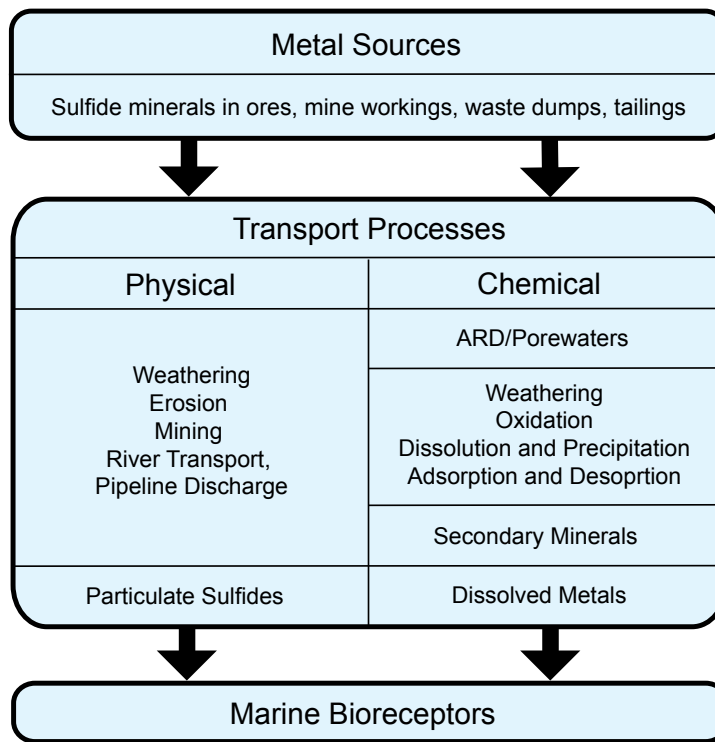


Figure 2. A schematic illustration of metal dispersion from source rocks (sulfide minerals) to marine biota (bioreceptors). ARD = acid rock drainage. Adapted from Balistrieri et al. (2007)

Table 1. Metal sources: Sulfide and secondary minerals

Mineral	Formula	Trace Elements*
<b>Sulfide Minerals</b>		
Pyrite	FeS <sub>2</sub>	Ni, Co, As, Cu, Zn, Ag, Au, Tl, Se, V
Pyrrhotite	Fe <sub>1-x</sub> S	Ni, Co, Cu
Chalcopyrite	CuFeS <sub>2</sub>	Ag, Au, In, Tl, Se, Te
Sphalerite	ZnS	Mn, Cd, Hg, In, Tl, Ga, Ge, Sb, Sn, Pb, Ag
Galena	PbS	Ag, Cu, Fe, Bi
Arsenopyrite	FeAsS	Ag, Au, Co, Sn, Ni Sb, Bi, Cu, Pb
<b>Secondary Minerals</b>		
Goethite	α-FeO(OH)	Mn
Ferrihydrite	Fe <sub>5</sub> O <sub>3</sub> (OH) <sub>9</sub>	—
Schwertmannite	Fe <sub>8</sub> O <sub>8</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>	—
Jarosite	KFe <sub>3</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>	Ag, Pb
Melanterite	FeSO <sub>4</sub> •7H <sub>2</sub> O	Cu
Eriochalcite	CuCl <sub>2</sub> •2H <sub>2</sub> O	—

\*Trace element data from <http://www.mindat.org>



Figure 3. View westward across degraded sulfide-bearing waste rocks at the Beatson mine site, Alaska. Erosion and oxidation of the waste piles result in dispersal of sulfide particles and dissolved metals into Prince William Sound. Copper was mined from the Beatson deposit between 1904 and 1930.

be transported far downstream from mine sites and into estuarine environments. A study by Leblanc et al. (2000) reports an example of this long-distance transport. They determined that two pyrite- and metal-rich (Pb, Ba, As, Cu, Zn, Sn) sand horizons in a sediment core retrieved from the upper Rio Tinto estuary, Spain, are flood deposits. This river flows past mines of the southern IPB. The deeper sulfide horizon was dated by <sup>14</sup>C methods at ~ 2,500 years BCE, which corresponds to Copper Age mining; the upper, near-surface horizon is derived from modern (late nineteenth century to present) mining activities (Leblanc et al., 2000). Clastic pyrite and other particulates were reworked down river about 100 km to the estuary during storm events.

The catastrophic failure of tailings impoundments can cause rapid displacement of large amounts of particulate sulfide with large-scale impact on the coastal environment, economic activities, and public health (Plumlee et al., 2000; Mateos, 2001). In 1996, more than  $1.6 \times 10^6 \text{ m}^3$  of tailings stored in an open pit at the Marcopper copper mine near the center of Marinduque Island, Philippines, were suddenly released into the Boac River; ultimately, as much as  $260,000 \text{ m}^3$  of reworked tailings enriched in Cu, Zn, Pb, and Mn were deposited in a sedimentary apron extending offshore up to 2 km beyond the river mouth (David, 2002). Two years later, the failure of the tailings impoundment at the Los Frailes zinc mine in the IPB near Aznalcóllar resulted in release of about  $5.5 \times 10^6 \text{ m}^3$  of acidic water and  $1.3 \times 10^6 \text{ m}^3$  of pyrite-rich tailings into the nearby Guadiamar River and further downstream into the Guadalquivir

estuary on the southwest Spanish coast (Hudson-Edwards et al., 2003).

A third mode of physical transport affecting coastal marine environments is the intentional channeling of tailings to disposal sites in shallow water offshore. Three notable examples illustrate the practice. First, on Marinduque Island, an estimated 200 million tons of tailings from the Marcopper porphyry copper deposit were discharged over a 16-year period (1975–1991) into shallow waters of Calancan Bay (Coumans and MACEC, 2002). Over that time period, waste discharge was delivered first from the beach and then from the end of a four-kilometer-long tailings causeway built across Calancan Bay. The causeway and surrounding submarine tailings outfall cover much of the bay and at least 60 km<sup>2</sup> of adjacent seafloor (Ellis et al., 1994). A second example is that for about 50 years (1938–1989), pyrite-rich tailings from two porphyry copper mines (El Salvador and Poterillos) in northern Chile were funneled more than 100 km down the El Salado River and into the Pacific Ocean at Chañaral Bay and a nearby cove, Caleta Palito. The approximately 150 million tons of tailings entering Chañaral Bay formed a beach deposit, 10 to 15 m thick, that displaced the shoreline one kilometer westward (Figure 4; Castilla, 1983; Wisskirchen and Dold, 2006). The exposure of tailings to strong onshore winds has resulted in a field of unstable “tailings dunes” (Neary and Garcia-Chevesich, 2008). A third example of extreme pollution related to offshore tailings disposal occurs at Portman Bay on the Mediterranean coast of Spain. Although Portman Bay and the surrounding area had experienced environmental stresses



Figure 4. Aerial view of beach deposit composed of mine tailings in Chañaral Bay, Chile. The width of the beach (shown at bracket) is approximately one kilometer. The city of Chañaral is in the lower right part of the photograph.

from mining since Roman times, by far the greatest impact occurred during the period 1957–1991 when nearly 60 million tons of tailings from nearby Pb-Zn mines at La Union were pumped directly into the bay. As at Chañaral Bay, one can walk across Portman Bay on mine waste. Mineralogical studies of sediment samples from Portman Bay show that pyrite contents exceed 10% (Martinez-Sánchez et al., 2008).

### CHEMICAL PATHWAYS

**Sulfide Oxidation, Mobilization of Metals, and Formation of ARD**  
The colorful reddish-brown waters emanating from thousands of abandoned mines, sulfide-bearing waste piles, and tailings impoundments provide highly visible examples of ARD (see photo on page 172). ARD is caused by chemical reactions between sulfide minerals in

rocks and oxygenated surface waters, the end result of which is breakdown of the sulfides and acidification of fluids (fluid pH values range from  $-3.5$  to  $5$ ; Nordstrom and Alpers, 1999). The exposure of sulfide minerals to oxygen and water may take place naturally during erosion and weathering. However, ARD is exacerbated by increased exposure of sulfides brought about by mining. Sulfide minerals are formed in oxygen-poor, reducing environments; thus, they are inherently unstable in the presence of oxygen. Abiotic oxidation rates vary among the sulfides with a general order of reactivity: pyrrhotite > galena – sphalerite > pyrite – arsenopyrite > chalcopyrite (Jambor, 1994). Thus, pyrrhotite is the most readily oxidized, whereas chalcopyrite is relatively resistant to weathering. Because pyrite and pyrrhotite are dominant minerals in

many deposits and are also abundant in mine tailings (Blowes et al., 2003), the oxidation of Fe sulfides is a leading contributor to ARD (Nordstrom and Alpers, 1999). For example, the oxidation of pyrite by molecular oxygen in groundwater (Reaction 1) generates hydrogen and sulfate ions in solution that combine to form sulfuric acid. A second reaction, however, is important to the oxidation process: the oxidation of ferrous iron to ferric iron (Reaction 2) that is stable in low-pH conditions. Ferric iron is a powerful oxidant for sulfides, including chalcopyrite (Reaction 3). Ferric iron can also be hydrolyzed under less-acidic conditions to form Fe oxyhydroxide minerals, the reddish precipitates associated with ARD (see photo on page 172).

It is now well known that acidophilic, iron-oxidizing bacteria such as *Acidithiobacillus ferrooxidans* have a catalyzing effect on sulfide oxidation, particularly the conversion of ferrous to ferric iron (see reviews by Mills, 1999; Nordstrom and Alpers, 1999; and Gould and Kapoor, 2003). Laboratory tests indicate that the presence of bacteria may increase the rate of ferrous iron oxidation by five orders of magnitude compared to abiotic oxidation (Singer and Stumm, 1970).

#### Metal Fluxes in the Marine Environment

The acidity and metal load of ARD or pore waters in submarine tailings reflect the type of ore deposit, amount of

pyrite and/or pyrrhotite, and overall abundances of metals in the source rocks (Plumlee, 1999). Ferrous iron ( $\text{Fe}^{2+}$ ) and other divalent metals ( $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Pb}^{2+}$ ) are soluble and thus highly mobile in surface waters as long as acidic conditions prevail. For example, the ARD-impacted Rio Tinto draining the IPB maintains low pH levels ( $< 4$ ) and carries high concentrations of dissolved metals into its estuary along the Atlantic Ocean (Achterberg et al., 2003). The dissolved metal loads of the Rio Tinto (and a companion river, the Rio Odiel) are large: up to 7,900 tons of Fe, 3,500 tons of Zn, and 1,700 tons of Cu per year (Oliás et al., 2006). The result is a regionally important chemical plume with elevated levels of Cu and Zn that extend southeastward along the coast of Spain and through the Strait of Gibraltar (Figure 5; van Geen et al., 1997; Elbaz-Poulichet et al., 2001a,b). It is believed that contamination in rivers flowing from the IPB is a principal cause of elevated metal concentrations in the

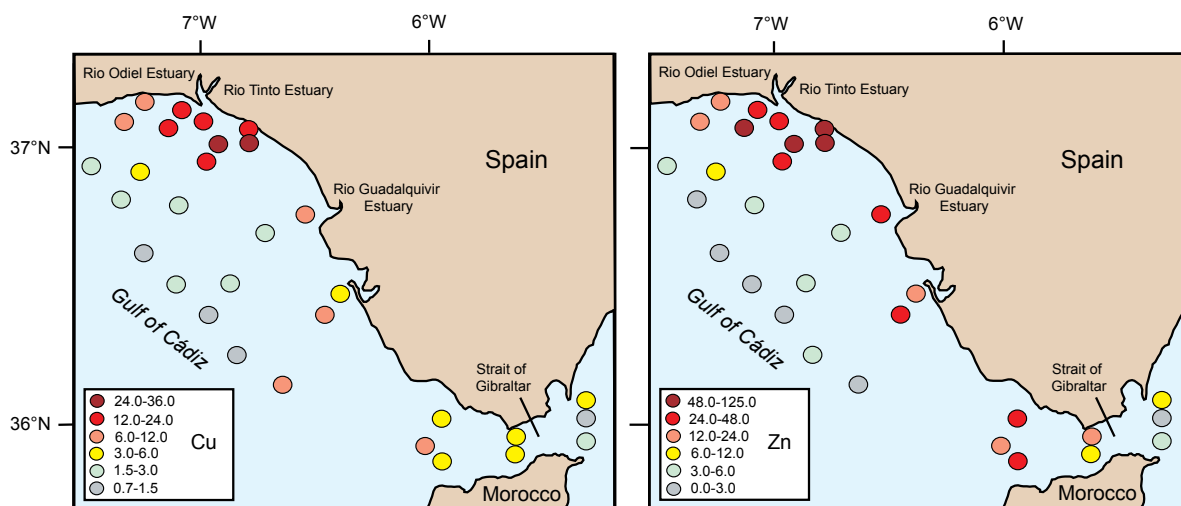
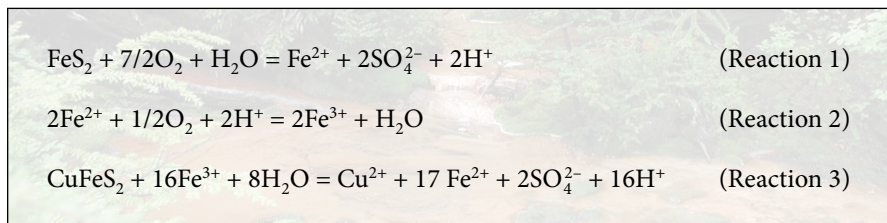


Figure 5. Cu and Zn concentrations in surface waters of the Gulf of Cádiz (modified from Elbaz-Poulichet et al., 2001b). The units are  $\text{nmol kg}^{-1}$ . The plume of metal-enriched seawater flows southeastward along the coast and through the Strait of Gibraltar into the Mediterranean Sea. The metals, derived from sulfide deposits in the Iberian Pyrite Belt, are mobilized in acid rock drainage into local watersheds and then transported in solution to coastal estuaries and the Gulf of Cádiz by the Rio Odiel and Rio Tinto.



Mediterranean Sea more than 300 km away (van Geen et al., 1988).

The oxidation of sulfides in submarine tailings can also result in partitioning of metals into interstitial fluid. For example, Plumlee et al. (2000) reported high levels of metals relative to seawater in pore water samples cored from the tailings causeway in Calancan Bay (Figure 6). Values for As, Cu, Se, and Ag exceed the US Environmental Protection Agency (EPA) exposure limits for seawater (US Environmental Protection Agency, 2009). Similarly, Dold (2006) and Wisskirchen and Dold (2006) analyzed extremely high Cu concentrations (to 2265 mg L<sup>-1</sup>) in pore water samples from oxidized tailings at Chañaral Bay. At the Ellamar copper deposit in Prince William Sound, Alaska, a sulfide-rich debris pile left behind after mine closure in the 1930s is preserved as a component of intertidal beach gravels (Koski et al., 2008). The Fe sulfide-rich clasts are undergoing oxidation with consequent acid generation in the gravels.

Analyses of the interstitial fluid indicate a mixture of seawater and groundwater, low pH (to 2.9), and elevated concentrations of Cu (to 18.4 mg L<sup>-1</sup>), Zn (to 7.0 mg L<sup>-1</sup>), Pb (to 2.0 mg L<sup>-1</sup>), and Hg (to 4.1 µg L<sup>-1</sup>).

The precipitation of secondary minerals also plays a major role in the dispersion and attenuation of metals in ARD (Nordstrom and Alpers, 1999) and, similarly, during oxidation of submarine tailings (Bea et al., 2010). There are two important groups of secondary minerals: (1) relatively insoluble ferric oxyhydroxides and hydroxysulfates, and (2) highly soluble sulfates and chlorides (Table 1). With increasing pH (resulting, for example, from mixing of acidic fluid

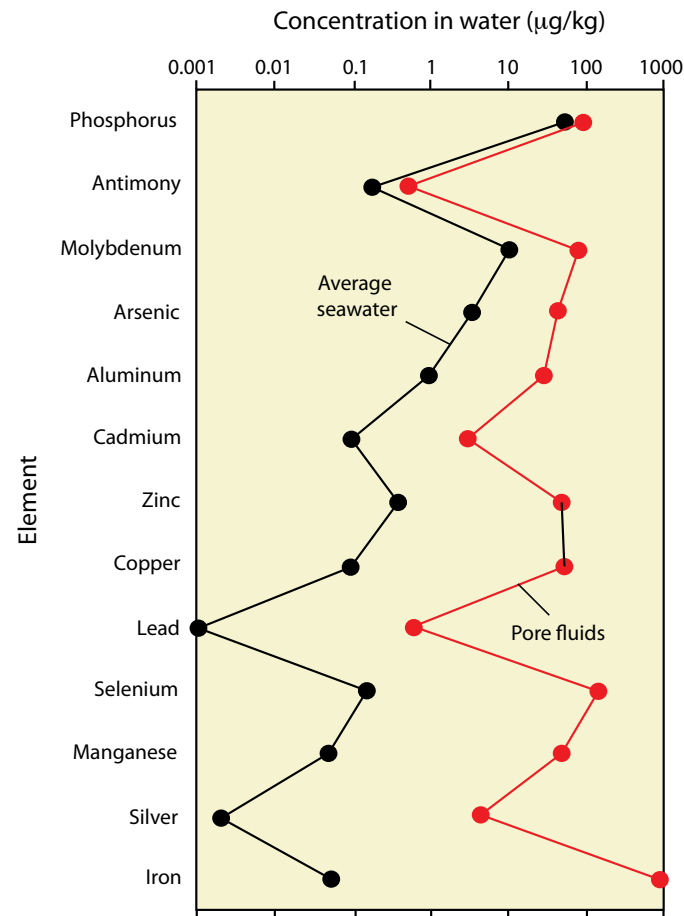


Figure 6. Plot showing elevated element concentrations in pore waters from Calancan Bay tailings compared to their concentrations in uncontaminated seawater (after Plumlee et al., 2000). The metal enrichments result from oxidation of sulfide particles in the tailings.

with freshwater or seawater), Pb, Cu, and Zn in solution are readily adsorbed onto the surface of newly formed Fe oxyhydroxide solids (Smith, 1999). This partitioning of metals between dissolved and particulate phases has been documented in both fresh and saline waters (Balistrieri and Murray, 1982; Johnson, 1986; Featherstone and O'Grady, 1997), and should be an important metal trap in mixing zones between ARD (or tailings pore waters) and seawater in near-shore environments. It is also likely that a significant fraction of the total metal load in ARD-impacted rivers like the Rio Tinto, which exhibit a gradual rise in pH toward the estuary, is carried by particulate Fe oxyhydroxides. The deposition of

these particles in river and estuary sediments may reduce the flux and bioavailability of metals.

The hydroxysulfate mineral jarosite is another important secondary mineral because of its metal-absorbing capacity and stability at low pH. At Portman Bay, Spain, for example, jarosite proved to be very resistant to metal leaching during sequential extraction investigations conducted by Martínez-Sánchez et al. (2008). Jarosite has also been reported in oxidized tailings at Chañaral Bay (Wisskirchen and Dold, 2006) and is an abundant precipitate within beach gravels at the Ellamar mine site in Prince William Sound (Koski et al., 2008).

Soluble sulfate minerals, precipitated

by evaporation of ARD, are temporary repositories for metals during transport. These efflorescent salts are easily dissolved by rainwater and groundwater to create another acidic, metal-rich fluid. The impact of secondary sulfates on metal fluxes is recognized in the enormous increases in metal load-

seawater, and enrichment of Cu in pore fluids—induce the precipitation of the copper chloride mineral eriochalcite ( $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ ). Reactive transport modeling by Bea et al. (2010) suggests that capillary flow and high evaporation rates on the tailings' surface exert major controls on chloride mineralization. Because

mine-impacted coastal environments. Perhaps the most direct method is analysis of metals in sessile and burrowing marine organisms at sites of ARD. Koski et al. (2008) reported elevated metal concentrations (to  $86 \text{ mg kg}^{-1}$  Cu,  $304 \text{ mg kg}^{-1}$  Zn, and  $3.0 \text{ mg kg}^{-1}$  Pb) in soft tissue from mussels (*Mytilus edulis*) collected near copper mine sites in Prince William Sound. For comparison, Cu, Zn, and Pb concentrations in mussels from uncontaminated sites of southern coastal Alaska, reported by the Mussel Watch Project, are typically  $< 10$ ,  $< 100$ , and  $< 1 \text{ mg kg}^{-1}$ , respectively (National Oceanic and Atmospheric Administration, 2011). Elsewhere, soft tissue samples in clams from the Callahan mine site have Pb concentrations as high as  $43 \text{ mg kg}^{-1}$  (Ayuso and Foley, 2009), an amount that greatly exceeds the tolerance level for Pb in shellfish ( $1.7 \text{ mg kg}^{-1}$ ) listed by the US Food and Drug Administration (1993). In tropical settings, growth rings in reef corals are sensitive recorders of seawater chemistry, and also provide high-resolution information (based on yearly variations in oxygen isotope ratios or trace element concentrations) about the time period of pollution. Thus, reef samples of *Porites* from Marinduque Island were found to have anomalous Cu concentrations in growth rings that are temporally coincident with the 1996 tailings spill in the Boac River (David, 2003). The Cu-enriched coral was sampled at a reef located 2.5 km from the Boac River mouth. In a similar study at Misima Island, Papua New Guinea, Fallon et al. (2002) reported increased levels of Zn and Pb (to 80 and 6 times the normal concentrations in growth rings, respectively) in *Porites*

“ THE PATHWAYS APPROACH ADOPTED HERE CONSIDERS A NUMBER OF PHYSICAL AND CHEMICAL PROCESSES THAT INFLUENCE DISPERSION OF METALS IN THE CONTINUUM FROM METAL SOURCE TO BIORECEPTOR. ”

ing recorded in the Rio Tinto as ARD was “flushed out” in the first rains after the dry season in 2004. According to Cánovas et al. (2008), 770 tons of Fe, 100 tons of Cu, and 100 tons of Zn were carried by the river toward the estuary during a one-month period, one of the largest loads ever recorded in an area influenced by ARD. This dissolved element load was as much as 8,200 times greater than monthly totals during the summer dry season of 2004.

Although soluble sulfate precipitates are commonly associated with ARD on land, conditions in submarine mine tailings may favor the deposition of secondary chloride minerals. A well-documented example of secondary chloride occurs at Chañaral Bay (Dold, 2006; Bea et al., 2010). There, several factors—exposure of the sandy tailings above the high tide line, extreme aridity (Atacama Desert), infiltration of

of the persistent strong onshore winds at Chañaral Bay, eolian transport of metal-enriched sand and efflorescent salts from the tailings present an additional health hazard to inhabitants of Chañaral and the surrounding area (Neary and Garcia-Chevesich, 2008).

### BIOACCUMULATION

The final pathway segment is the bioaccumulation of metals by aquatic plants and animals in mining-impacted coastal zones. Processes occurring at this stage provide entry points into the food chain, with environmental and toxicological implications for entire ecosystems, including human populations living in these areas.

#### Evidence for Bioaccumulation

Several analytical methods have been used to determine that bioaccumulation of metals has, in fact, occurred in

from fringing reefs; the formation of the enrichments correlate in time with commencement of gold mining on the island and a subsequent increased rate of sedimentation.

Lead isotope ratios have proved to be an effective fingerprinting tool in environmental research (Komárek et al., 2008), and this method has recently been applied to assess the bioaccumulation of metals in coastal zones influenced by mining activity. Ayuso and Foley (2009) determined Pb isotope ratios for massive sulfide ores, mine waters, estuary sediment, and unmineralized country rocks from the Callahan mine site as well as for hard parts of clams, crabs, and lobsters from the contaminated estuary (Figure 7). The overlap in ranges of Pb isotope ratios indicates that at least some of the Pb in the biota was derived from sulfide minerals. An investigation of marine biota from a fjord near the Black Angel Pb-Zn mine in western Greenland also demonstrates the value of Pb isotopes as tracers for metal sources (Søndergaard et al., 2010). Their analyses revealed that ore-lead fractions in mussels and seaweed range from > 90% within 1 km of the mine to > 50% at a site 12 km away; at equal distances from the mine, the fraction of Pb derived from the sulfide ores in seaweed exceeded the fraction in mussels.

### Metal Bioavailability

The bioavailability and potential toxicity of metals in aquatic systems are, to a large extent, a function of their speciation (Tessier and Turner, 1995; Reeder et al., 2006). Bioavailability is further linked to specific uptake pathways such as adsorption from dissolved species and ingestion of particles (Wang and Fisher,

1999). The bioavailability of dissolved copper has been investigated along the coastline at Chañaral Bay where seawater samples with total dissolved copper concentrations up to  $48 \mu\text{g L}^{-1}$  are correlated with the distribution of tailings (Stauber et al., 2005; Andrade et al., 2006). In this high-energy marine setting, that amount of copper greatly exceeds the amount that can be accommodated by less-labile organic complexes; hence, a significant fraction (> 50%) of the total dissolved copper is potentially available as free ions ( $\text{Cu}^{2+}$ ) for uptake by marine organisms. The impact of high copper concentrations on marine biota at Chañaral Bay is described in the next section.

Metal speciation and bioavailability in estuaries are more complex and

less predictable owing to geochemical variations in organic-rich sediment. In a lengthy review, Bryan and Langston (1992) cited a number of processes that influence bioavailability in sediment-dominated environments, including mobilization of metals into pore fluids, transformation to bioavailable organic species (e.g., by methylation), adsorption by iron oxide and organic particles, competition for metal uptake sites in organisms, and bioturbation. Bioavailability of metals in estuarine settings is also related to disturbance events (Eggleton and Thomas, 2004), feeding behavior of aquatic animals (Lee et al., 2000; Griscom and Fisher, 2004), and particle size (Thorne and Nickless, 1981). There is evidence for the persistence of

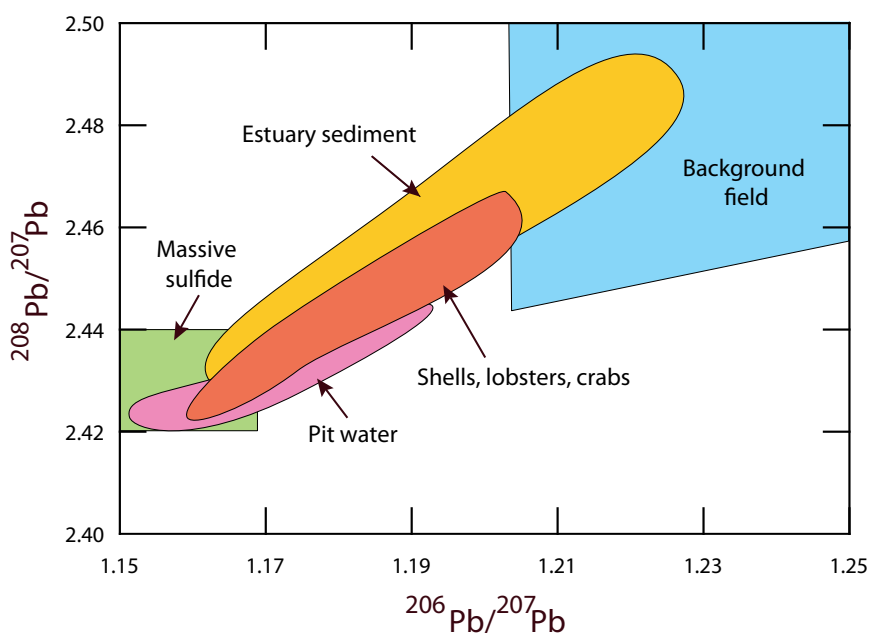


Figure 7. Lead isotope data for rocks, water, sediment, and biota at the Callahan mine site, Maine (Ayuso and Foley, 2009). The individual fields represent the range of data for massive sulfides from the Callahan deposit (green), sediment from the Goose Pond estuary (gold), water from the flooded open pit (pink), hard parts of marine bivalves and crustaceans (orange), and unmineralized sedimentary and volcanic rocks (background field, blue). The trend of isotope ratios for bivalves, lobsters, and crabs indicates the presence of lead from massive sulfides as well as lead from background sources. Similarly, Pb in pit water and estuary sediment appears to be a mixture derived from mineralized and unmineralized sources.

bioavailable metals in estuarine environments over time. In a study of mine-impacted estuaries in England, Rainbow et al. (2011) showed that metals (Cu, Pb, Zn, As, Ag) measured in selected bio-monitors (algae, worms, and mollusks) remained high relative to regional base-line levels for more than a century after cessation of mining.

### Impact on Biota

It is now well documented that increased levels of metals related to anthropogenic activities such as mining can have a substantive impact on marine biota in coastal environments (e.g., Marsden and DeWreede, 2000; Grout and Levings, 2001; Burd, 2002; Elberling et al., 2003). In field studies, however, deleterious or toxic effects related to specific metal contaminants are often less obvious (Bryan and Langston, 1992), and in many

feeding strategies, storage capacities, and elimination efficiencies for various organisms (Langston and Spence, 1995). A widely used laboratory-based toxicity test involves exposure of marine invertebrates at embryo and larval stages to contaminated sediment pore water or seawater. In an application of this technique using sea urchins, Carr et al. (2003) identified acute toxic levels of Cu and Zn (sufficient to prevent reproduction) in pore fluids within tailings at Calancan Bay. Likewise, at Portman Bay, Cesar et al. (2004) reported a 100% sea urchin larval mortality for pore waters in all sediment samples to water depths of 80 m; toxicity was only slightly less when water from the sediment-water interface was used in the experiments. Cesar et al. (2004) concluded that benthic communities will be greatly stressed by any disturbance of the tailings, whether it results

and lower abundance and diversity of invertebrate fauna.

Conditions at Chañaral Bay—large volumes of copper mine tailings in a high-energy coastal environment, relatively low organic matter, and absence of other pollutants—are favorable for a systematic ecotoxicological assessment of impact focused on bioavailable copper. Environmental changes include (1) proliferation of the green algae *Enteromorpha compressa* (Fariña and Castilla, 2001), (2) decreased abundance and diversity of algae and sessile invertebrates (Medina et al., 2005), and (3) lower density and taxa diversity of meiofauna, except for the copper-tolerant otoplanid turbellarians (Lee and Correa, 2005; Lee et al., 2006).

### SUMMARY

Metal fluxes related to mining and other industrial activities impact coastal zones in many countries. The pathways approach adopted here considers a number of physical and chemical processes that influence dispersion of metals in the continuum from metal source to bioreceptor. The sources of metals, sulfide minerals in ores, mine dumps, or tailings, may occur in or adjacent to the littoral zone (Prince William Sound, Callahan mine) or hundreds of kilometers inland from the shoreline (IPB). Large quantities of metals are physically dispersed during intentional or accidental transport of mine tailings into the shallow offshore environment (Marinduque Island, Chañaral Bay, Portman Bay). At mine sites on land, the oxidation of sulfide minerals, especially pyrite and pyrrhotite, generates acidity and initiates transportation of dissolved metals in the form of ARD. In streams

“...A GROWING APPRECIATION FOR BROADER ECOLOGICAL IMPACTS OF METAL CONTAMINATION HAS LED TO COMPLEMENTARY METHODOLOGIES THAT INCLUDE LABORATORY TOXICITY TESTS... AND FIELD-ORIENTED STUDIES OF SPECIES RICHNESS AND BIODIVERSITY.”

cases, nonlinear or inverse relationships between metal exposure concentrations and bioaccumulation have been reported (McGeer et al., 2003; DeForest et al., 2007). The latter findings reflect the influence of biological factors such as the permeability of external surfaces,

from storm activity or dredging. In a more integrated ecological approach, Cesar et al. (2009) determined that concentration gradients for Zn, Pb, and Fe in sediments surrounding Portman Bay are positively correlated with toxicity (as measured by sea urchin mortality tests)

and rivers dominated by ARD, metals may be carried in solution far downstream to the mixing interface between freshwater and seawater (Rio Tinto and Rio Odiel estuaries) and beyond to the coastal ocean (Gulf of Cádiz). In submarine tailings, a similar process occurs in which the weathering of particulate sulfides leads to partitioning of metals into pore waters and seawater. Dispersion of metals in solution may be affected by adsorption onto surfaces of secondary minerals (e.g., Fe oxyhydroxides) following an increase in pH, or precipitation as highly soluble salts (sulfates, chlorides) where metal-rich fluids evaporate to dryness. These secondary minerals also have environmental consequences. Insoluble oxyhydroxides can remove metals from solution and bioavailability. Conversely, the redissolution of soluble salts during rain events can flush large quantities of metals into the marine environment (IPB). Furthermore, efflorescent secondary minerals formed on partly submerged mine tailings (Chañaral Bay) are subject to eolian transport into populated areas.

Metal uptake by marine biota (and entry into the food chain) represents the final pathway segment. There is a considerable amount of direct evidence for bioaccumulation in local organisms: anomalous metal concentrations in burrowing and sessile indicator species such as mussels, clams, and seaweed, and metal enrichments of reef corals in tropical settings. Recent studies reveal overlapping patterns of Pb isotope ratios for sulfide ores and local organisms, including bivalves, crustaceans, and seaweed, all proof that the biota have incorporated metal from sulfide deposits. Bioavailability and potential toxicity

in aquatic environments are, to a large extent, a function of metal speciation. The bioavailability of metals in estuarine environments, however, is more complicated owing to geochemical variations in organic-rich sediments, partitioning of metals into pore waters, adsorption by iron oxide and organic particles, feeding behavior of aquatic animals, formation of bioavailable organic compounds, and variations in particle size. Finally, a growing appreciation for broader ecological impacts of metal contamination has led to complementary methodologies that include laboratory toxicity tests (e.g., sea urchin mortality) and field-oriented studies of species richness and biodiversity.

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