Chapter 1—Introduction to Pathways of Metal Transfer from Mineralized Sources to Bioreceptors

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Since 1995, the Mineral Resources Program of the U.S. Geological Survey has funded a number of studies in the western United States that address environmental issues associated with mineral deposits. Projects with environmental components in the western United States include Geoenvironmental Impacts of Hg and As; Humboldt River Basin Assessment; Coeur d'Alene Life-Cycle Models; Southwest Mineral and Environmental Investigations; and Geologic and Geoenvironmental Studies of the Western Phosphate Field. Toxicity to humans and other biota is a primary issue in these studies. Such toxicity is related to high concentrations of environmentally significant elements released during natural weathering prior to mining, during mining of mineral deposits, and during modern weathering of historic mine wastes. Environmentally significant elements, including but not limited to Al, As, Cd, Cu, Fe, Hg, Mo, Pb, Sb, Se, and Zn, are defined to be elements that are essential to or adversely impact the health of organisms. Allowable concentrations of many environmentally significant elements are regulated by state and Federal agencies. Toxicity is also related to the speciation and location of elements in the ecosystem. The term "speciation" in this context means the exact chemical forms in which an element occurs and the quantitative distribution of different coexisting forms.

Results of these studies provide a scientific basis for local, state, and Federal agencies charged with minimizing the impacts of trace and potentially toxic elements on the environment and health of biota to make decisions, develop strategy, and assess mitigation alternatives. As some of these projects draw to a close, we want to summarize, in a consistent manner, the results of these studies, identify gaps in our knowledge, and propose topics for future research. This collection of papers aims to meet those goals.

The common themes among the various environmental studies are (1) determining the distributions and concentrations of environmentally significant elements throughout the study areas, (2) understanding how elements move through the environmental systems, and (3) identifying the relationships between geochemical behavior of these elements and impacts on biota. These themes provide a framework for examining and comparing the various studies.

This framework or conceptual model, presented in figure 1, has the advantage of being transferable among ecosystems of widely varying scales. It is composed of three linked components: *source*, *processes*, and *bioreceptors*. The source component includes natural and anthropogenic entities such as mineralized terranes, mineral deposits and mines, mine tailings, and waste rock. Characterization of the source component involves determining the concentrations of elements in the source, identifying the phases where trace elements reside, assessing the speciation of the trace elements (for example, oxidation state and type of bonding to the mineral structure), and determining the rates and mechanism of release from the source.

The processes component of the model includes all of the physical and biogeochemical processes that act either to redistribute or chemically transform trace elements among sources and secondary phases. For example, particulate phases such as mine tailings can be physically moved away from the source by hydrologic transport, taken up by bioreceptors (for instance, ingestion of particulate Pb by humans or birds), or transformed into dissolved species by oxidation, reduction, dissolution, or desorption and exchange reactions. Dissolved species can be physically transported by advection or diffusion away from the source, taken up by bioreceptors (for instance, assimilation of methyl mercury by algae), or incorporated into particulates through precipitation and adsorption reactions. The cycling of elements between particulate and dissolved phases is a recurring process in a given ecosystem.

The third component of the model is bioreceptors (including humans, livestock, wildlife, plants, and microorganisms). Information in this component addresses the biogeochemical factors (for example, molecular speciation of elements in host phases and mechanisms of uptake) that control the accessibility and availability of trace elements to biota.

Using this three-component conceptual framework, table 1 presents an overview of the individual study areas, summarizing their locations; characteristics (that is, deposit types, ecoregions and climates, elements of interest, and relative ranges of pH); documented processes operating within the systems; bioreceptors and probable mechanisms of uptake; and topics that need further research. These studies encompass a range of deposit types, climate regimes, and elements of interest. Many of the critical processes affecting element distributions and behavior are similar in these diverse environments and include those related to physical movement (for example, aeolian transport, erosion, hydrologic transport and mixing, and fluxes across interfaces) and to transformations between dissolved and particulate phases (for example, adsorption and desorption, mineral precipitation and dissolution, and organic matter production and oxidation). Microorganisms mediate many of the geochemical reactions. Bioreceptors that have been identified in these systems include humans, livestock, game animals, fish, amphibians, birds, aquatic and benthic invertebrates, and plants.

The chapters that follow discuss the geologic setting of each study area and answer the following questions, most of which are directly related to the conceptual framework:

1. What is known about the distributions, concentrations, and speciation of environmentally significant elements in the system?
2. What is known about the processes that mobilize elements from their sources and then act to physically and biogeochemically redistribute them?
3. What is known about impacts to biota, and can specific processes be identified that influence the accessibility or availability of trace elements, acid, and other chemical species to biota?

4. What are the major gaps in knowledge (that is, new directions for research) remaining from the study?

The ability to answer the above questions varies among study areas because of the scope of ongoing work, the level of involvement of collaborative partners, and the length of time that research has been done. One study is just starting, whereas others are in their fifth or sixth year of study.

From examination of this collective work, we propose to focus our future research on the processes component of the conceptual model. The following research themes have been identified:

1. Speciation of dissolved and solid phases and the influence of speciation upon geoavailability (that is, biogeochemical mobility and accessibility) and bioavailability (that is, uptake by humans and wildlife) of trace elements.
2. Microbial activities and transformations.
3. Processes at physical, geochemical, and biological interfaces.
4. Precipitation and transformations of metal oxyhydroxides and metal oxyhydroxysulfates and associated interactions with trace elements.
5. Physical transport and dispersion of trace elements.
6. Conceptual and quantitative modeling of element behavior in mineralized ecosystems and understanding how elements and ecosystems respond to natural and anthropogenic perturbations.

Research to address these themes is now being done in the Pathways Project, which is funded by the Mineral Resources Program. Specific tasks of the Pathways project (and the related themes from above) include:

1. Impact of Hg from placer gold mine tailings on bioreceptors (themes 1 and 2).
2. Biogeochemical and biochemical pathway investigations of Cd in subarctic ecosystems using a hyperaccumulator species (willow) (theme 1).
3. Effect of microbially mediated Fe, Mn, and SO_4 reducing conditions on Hg and As transformation in a historic mining environment (themes 1, 2, 3, and 4).
4. Mobility and bioavailability of As and Se in the Great Basin as a function of redox conditions (themes 1, 2, 3, and 4).
5. Modeling the underlying processes that determine the concentrations and distributions of elements in environmental systems as a function of time (themes 1 through 6).

Results from these tasks will advance our understanding of specific processes that link geoavailability of environmentally significant elements to bioavailability in large-scale systems where mineralized areas are a long-term source of metals and other elements to the systems. By determining the dominance and influence of particular physical, chemical, and biological processes that control metal mobility and accessibility to biota, we will be able to identify which specific processes should be targeted during remediation or management of these systems to best minimize the impacts of trace and toxic elements on the environment and the health of biota.

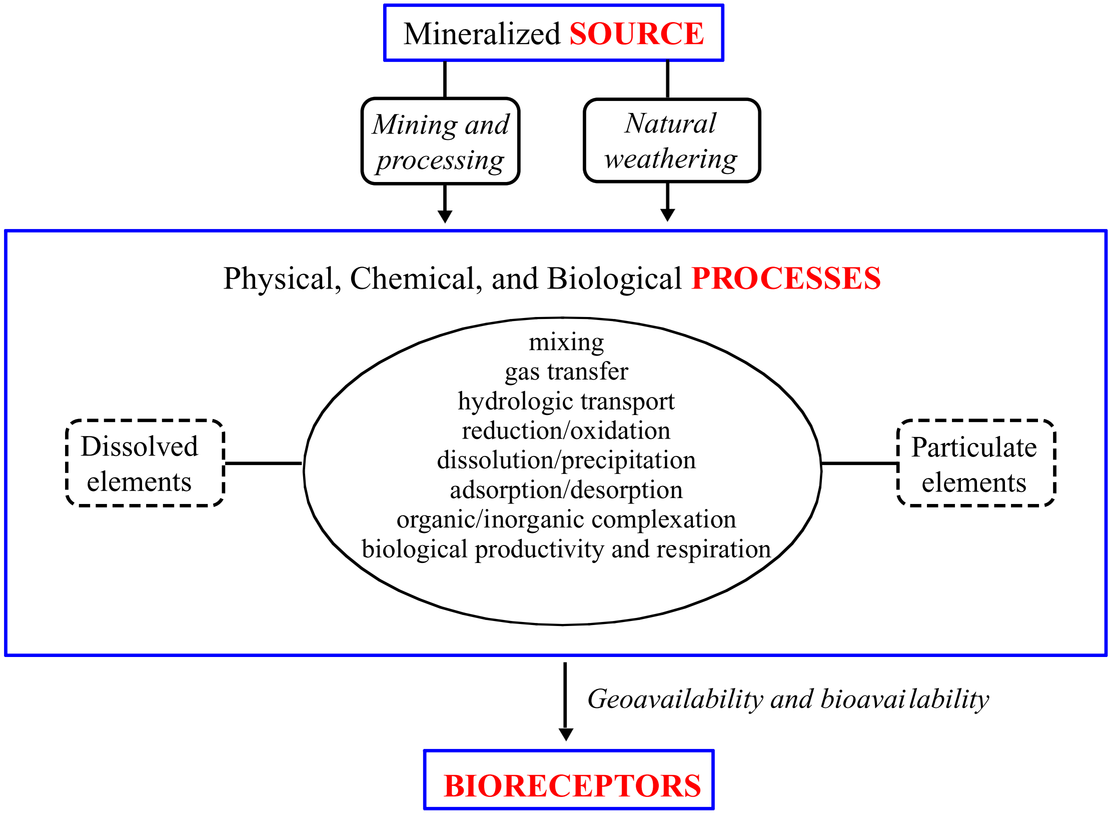

Figure 1. Conceptual model used to compare environmental studies. Processes determine whether an element is geoavailable and bio-available. Geoavailability and bioavailablity of elements determine whether they may be transferred to a bioreceptor in the system. See text for additional details.

Table 1. Summary of known characteristics, processes, bioreceptors, and knowledge gaps for each of the seven study areas evaluated in the Pathways Project.

[Deposit types are from Cox and Singer (Cox, D.P., and Singer, D.A., 1986, Mineral Deposit Models: U. S. Geological SurveyBulletin 1693, 379 p.); ecoregions and climate data are from Bailey (Bailey, R.G., 1995, Descriptions of the ecoregions of the United States:http://www.fs.fed.us/land/ecosysmgmt/, accessed Nov. 1, 2010.]

Study Area	**Deposit Type**	**Ecoregion; Climate**	**Elements; pH range**
Sierra, California (Mother Lode)	Placer Au; low-sulfide Au-quartz	Humid temperate domain, Mediterranean division-mountain provinces, Sierran Steppe-Mixed Forest-Coniferous Forest-Alpine Meadow Province; variable precipitation depending on location (250-1790 mm/yr), wet winters and dry, hot summers	As, Hg; acidic to neutral
Coast Ranges, California and Alaska	Hot-spring Hg; hot-spring Au-Ag; Si-carbonate Hg	*California*: Humid temperate domain, Mediterranean division-mountain provinces, California Coastal Range Open Woodland-Shrub-Coniferous Forest-Meadow Province; moderate precipitation (310-1020 mm/yr), mild rainy winters and hot, dry summers. *Alaska:* Polar domain, Tundra division; low precipitation (<200 mm/yr), very short, cool summers, long, severe winters, evaporation low, humid climate	Hg; neutral to alkaline
Yukon Tanana, Alaska (40-Mile and Good Paster drainages)	Placer Au; low-sulfide Au-quartz	Polar domain, Subarctic division, Upper Yukon Tayga Province; low precipitation (260-380 mm/yr), large annual temperature range, severely cold winters, short, hot summers	As, Cd, Hg; neutral
Humboldt River Basin, Nevada	Hot spring Au-Ag; hot-spring Hg; carbonate-hosted Au-Ag; placer Au	Dry domain, Temperate desert division, Intermountain Semidesert and Desert Province; low precipitation (130-490 mm/yr), evaporation > precipitation, hot summers, moderately cold winters	As, Se, Hg, Cd, Zn; neutral to alkaline
Coeur d'Alene River Basin, Idaho and Washington	Polymetallic vein	Dry domain, Temperate Steppe Division - Mountain Provinces, Northern Rocky Mountain Forest-Steppe-Coniferous Forest-Alpine Meadow Province; moderate precipitation (510-1020 mm/yr), severe winters, hot summer days and cool nights	Pb, Zn, Cd, Cu, As; acidic to neutral
Southwest Basin and Range, Arizona	Porphyry Cu; polymetallic vein	Dry domain, Tropical/Subtropical Desert Division, American Semidesert and Desert Province; low precipitation (valleys: 50-250 mm/yr, mountain slopes: <610 mm/yr), evaporation high, long, hot summers, moderate winters	As, Cd, Cu, Pb, Th, U, Zn; acidic
Southeast Idaho (Phosphoria Formation)	Black shale	Dry domain, Temperate Steppe Division, Great Plains-Palouse Dry Steppe Province; low precipitation (260-640 mm/yr), semiarid continental, cold, dry winters and warm to hot summers	Cd, F, Mn, Ni, Se, V, Zn; acidic to neutral

Table 1. Summary of known characteristics, processes, bioreceptors, and knowledge gaps for each of the seven study areas evaluated in the Pathways Project—Continued.

Study Area	**Known Sources: Mineralogy**	**Documented Processes**
Sierra, California (Mother Lode)	*Ores:* As in sulfide minerals *Tailings, waste rock, weathered ore:* oxidized Fe/Mn oxides, Fe sulfates, adsorbed and co-precipitated As *Ore processing:* Hg	Hydrologic transport Precipitation of oxides Adsorption Microbially-mediated redox Desorption related to recrystallization
Coast Ranges, California and Alaska	*Ores/waste rock:* meta-cinnabar (HgS), soluble Hg chlorides, oxides, sulfates *Retort soot:* elemental Hg	Evolution of ore processing technology Colloidal/particulate transport Co-precipitation Microbially-mediated transformations Vapor-phase evasion from soil and vegetation
Yukon Tanana, Alaska (40-Mile and Good Paster drainages)	*Loess:* Cd adsorbed to clay minerals and Ca/Mg carbonates	Precipitation of Fe/Mn oxides Adsorption Organic C mineralization
Humboldt River Basin, Nevada	*Ores/waste rock/tailings:* As and metal sulfide minerals	Evolution of ore processing technology Colloid-facilitated transport Evapotranspiration Microbially-mediated redox Anthropogenic inputs
Coeur d'Alene River Basin, Idaho and Washington	*Ores:* galena, sphalerite, tetrahedrite, siderite *River channel:* detrital metal sulfides and Pb carbonate *Levees:* authigenic Fe/Mn oxides and Pb/Zn sulfides, detrital ZnS, Pb carbonate *Wetlands:* authigenic Pb/Zn sulfides	Evolution of ore processing technology Hydrologic transport and mixing of waters Fluxes across interfaces Precipitation/dissolution Sorption Microbially-mediated redox Biological productivity/respiration
Southwest Basin and Range, Arizona	*Ore/waste piles/stream beds:* metal sulfides, Fe/Mn oxides	Hydrologic transport and mixing of waters Erosion Neutralization Precipitation/dissolution
Southeast Idaho (Phosphoria Formation)	*Shale:* apatites, pyrites, organic C *Waste dumps:* secondary minerals *Sediments:* Fe oxides, authigenic sulfides	Hydrologic transport Groundwater-surface water interactions Microbially-mediated redox Precipitation/dissolution Uptake by vegetation

Table 1. Summary of known characteristics, processes, bioreceptors, and knowledge gaps for each of the seven study areas evaluated in the Pathways Project—Continued.

Study Area	**Known Bioreceptors: Mechanisms of uptake**	**Knowledge Gaps**
Sierra, California Mother Lode)	*Humans:* drinking water *Fish:* ingestion, exposure *Birds*: ingestion	Ground water composition Role of biota in speciation and fate of elements Microbial activity Identity of organo-As species
Coast Ranges, California and Alaska	*Fish:* ingestion, exposure *Amphibians:* ingestion, exposure *Birds*: ingestion *Humans:* ingestion, possible inhalation	Predictive capability Links between biota and geology Integration of data and species from different ecosystems
Yukon Tanana, Alaska (40-Mile and Good Paster drainages)	*Willows:* uptake *Aquatic invertebrates:* ingestion *Fish:* ingestion, exposure *Birds:* ingestion *Moose:* ingestion	Speciation of elements Hg distributions and bioavailability Characterization of organic matter Links between biota and geology
Humboldt River Basin, Nevada	*Humans:* ingestion *Livestock:* ingestion *Migratory birds:* ingestion *Amphibians:* ingestion, exposure *Fish:* ingestion, exposure	Process-oriented studies Links between processes and bioreceptors
Coeur d'Alene River Basin, Idaho and Washington	*Humans:* ingestion *Fish:* ingestion, exposure *Migratory birds:* ingestion *Amphibians:* ingestion, exposure *Benthic invertebrates:* ingestion, exposure	Dynamic systems modeling of element behavior Response to natural and human-induced perturbations Links between geoavailability and bioavailability Role of microbes in element cycling
Southwest Basin and Range, Arizona	*Fish:* ingestion, exposure *Birds:* ingestion *Amphibians:* ingestion, exposure	Characterization of precipitates Behavior of U, As, Mo Chemical speciation Mineralogy of source material
Southeast Idaho (Phosphoria Formation)	*Game (elk/moose):* ingestion *Livestock:* ingestion *Birds:* ingestion *Fish:* ingestion, exposure *Benthic invertebrates:* ingestion, exposure	Modes of transport Importance of redox cycles Role of speciation in transport and bioavailability Microbial mediation of precipitation/dissolution