

Toxic Metals in the Environment: The Role of Surfaces

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Metals are prevalent in the environment. They are derived from both natural and anthropogenic sources. Certain metals are essential for plant growth and for animal and human health. However, if present in excessive concentrations they become toxic. Metals undergo an array of biogeochemical processes at reactive natural surfaces, including surfaces of clay minerals, metal oxides and oxyhydroxides, humic substances, plant roots, and microbes. These processes control the solubility, mobility, bioavailability, and toxicity of metals in the environment. The use of advanced analytical techniques has furthered our understanding of the reactivity and mobility of metals in the near-surface environment.

Keywords: critical zone, metals, sorption, surface complexation, biogeochemical processes

INTRODUCTION

Metals comprise about 75% of the known elements and can form alloys with each other and with nonmetals (Morris 1992). Metals have useful properties such as strength, malleability, and conductivity of heat and electricity. Some metals exhibit magnetic properties and some are excellent conductors of electricity. Metals are important components of our homes, automobiles, appliances, tools, computers and other electronic devices, and are essential to our infrastructure including highways, bridges, railroads, airports, electrical utilities, and food production and distribution (Hudson et al. 1999).

Civilization was founded upon the metals of antiquity, gold (Au), copper (Cu), silver (Ag), lead (Pb), tin (Sn), iron (Fe), and mercury (Hg). Metals were known to the Mesopotamians, Greeks, and Romans. Gold was first discovered about 6000 BC (Aicheson 1960; <http://neon.memphis.edu/cramb/processing/history.html>). Lead was produced before the rise of the Roman Republic and Empire. Since the beginning of the Industrial Age, metals have been emitted to and deposited in the environment. In some cases, metals have accumulated in terrestrial and aquatic environments in high concentrations and cause harm to animals and humans via ingestion of soil and/or dust, food, and water; inhalation of polluted air; and absorption via the skin from polluted soil, water, and air (Adriano et al. 2005). As the world's population and economies continue to grow, especially in developing countries, the need for metals will increase and so will the potential for soil and water contamination. This could have serious implications for human health and environmental quality.

Metals have traditionally been classified into categories such as light, heavy, semimetal (i.e. metalloids), toxic, and trace, depending on several chemical and physical criteria

such as density, weight, atomic number, and degree of toxicity (Roberts et al. 2005). Certain metals and metalloids are essential for plant growth and for animal and human health. With respect to plants, these are referred to as micronutrients and include B, Cu, Fe, Zn, Mn, and Mo. In addition, As, Co, Cr, Ni, Se, Sn, and V are essential in animal nutrition. Micronutrients are also referred to as trace elements since they are required in only small quantities, unlike major nutrients such as N, P, and K. In excess, trace elements

can be toxic to plants, microbes, animals, and humans. Problems also arise when there is a deficiency in essential elements.

Important trace elements in the environment are As, Ag, B, Ba, Be, Cd, Co, Cr, Cu, F, Hg, Mn, Mo, Ni, Pb, Sb, Se, Sn, Tl, V, and Zn. Trace elements in natural media are present at concentrations of less than 0.1%. In biochemical and biomedical research, trace element concentrations in plant and animal tissues are normally less than 0.01%. In food nutrition, a trace element is one that occurs at concentrations less than 20 mg kg⁻¹ (0.002% or 20 ppm). The term "heavy metals" refers to elements with densities greater than 5.0 g cm⁻³ and usually indicates metals and metalloids associated with pollution and toxicity; however, the term also includes elements that are required by organisms at low concentrations (Adriano 2001).

Thirteen trace metals and metalloids are considered priority pollutants (Table 1). They can be derived from both natural (geogenic) and anthropogenic sources. Natural sources include parent rocks and metallic minerals (metalliferous ores). Anthropogenic sources include agriculture (fertilizers, animal manures, pesticides), metallurgy (mining, smelting, metal finishing), energy production (leaded gasoline, battery manufacture, power plants), microelectronics, and sewage sludge and scrap disposal (Adriano 2001). Inputs of trace metals from various anthropogenic sources are given in Table 1 (Adriano 2001). Atmospheric deposition is a major mechanism for metal input to plants and soils. This is particularly true in forest ecosystems, where metal contamination of soils is almost totally due to atmospheric deposition. Volatile metalloids such as As, Hg, Se, and Sb can be transported over long distances in gaseous forms or enriched in particles, while trace metals such as Cu, Pb, and Zn are transported in particulate phases (Adriano 2001; Adriano et al. 2005). In terrestrial ecosystems, soils are the major recipient of metal contaminants, while in aquatic systems sediments are the major sink for metals. These contaminants can then impact freshwater and groundwater systems. Freshwater systems are contaminated due to runoff

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and drainage via sediments or disposal, while groundwater is impacted through leaching or transport via mobile colloids (Adriano 2001; Adriano et al. 2005).

BIOGEOCHEMICAL PROCESSES CONTROLLING METAL BEHAVIOR IN THE CRITICAL ZONE

Metals and metalloids undergo an array of dynamic biogeochemical processes in the critical zone, “the heterogeneous, near-surface environment in which complex interactions involving rock, soil, water, air, and living organisms regulate the natural habitat and determine the availability of life sustaining resources” (National Research Council 2001). Biogeochemical processes affect the speciation (form) of the metal, which in turn controls its solubility, mobility, bioavailability, and toxicity. Metal ions may enter the soil solution (the aqueous liquid phase of the soil and its solutes) and be subject to numerous pathways, all of which can potentially overlap (Fig. 1). The soil solution can contain metals as free ions or complexed to inorganic or organic ligands. Both the free ions and the metal–ligand complexes can be (1) taken up by plants, (2) retained on mineral surfaces, natural organic matter, and microbes, (3) transported through the soil profile into groundwater via leaching or by colloid-facilitated transport, (4) precipitated as solid phases, and (5) diffused in porous media such as soils. Root exudates and microbes affect the transport and solubility of metals. Microorganisms can transform metals such as Hg, Se, Sn, As, and Cr by means of oxidation–reduction and methylation (the process of replacing an atom, usually a H atom, with a methyl group) and demethylation reactions. These processes affect metal toxicity and mobility (Adriano 2001; Sparks 2002; Adriano et al. 2005; Morris 2005). For example, methylated (organic) forms of Hg are more toxic than inorganic forms of the element, and they bioaccumulate in organisms. Methylation is favored in environments characterized by low oxygen levels, low pH, and high soil organic matter (SOM) contents.

Metal Sorption

The sorption (retention) of metals, including alkali (e.g. K), alkaline earth (e.g. Ca), and transition (e.g. Cd and Ni) metals, on inorganic minerals (clay minerals, metal oxides and oxyhydroxides) and organic humic substances is one of the most important geochemical processes controlling the fate, transport, and bioavailability of metals in soil and water environments. Various metal sorption mechanisms can occur at natural surfaces, involving both physical and chemical processes (Fig. 2). (See also glossary on p. 190 for sorption vocabulary).

The most important adsorbents and sorbents for metals in natural systems such as soils and sediments are clay minerals and metal oxides and oxyhydroxides (Table 2), and humic substances associated with natural organic matter. These sorbents exhibit significant surface area and surface charge, which play a pivotal role in metal sorption. The surface charge can be neg-

TABLE 1
NATURAL AND ANTHROPOGENIC SOURCES AND COMMON FORMS
IN WASTES OF TRACE METALS ON THE PRIORITY POLLUTANT LIST

Element	Natural source or metallic minerals	Anthropogenic sources	Common forms in wastes
Ag	Free metal (Ag), chlorargyrite (AgCl), acanthite (Ag ₂ S), copper, lead, zinc ores	Mining, photographic industry	Ag metal, Ag–CN complexes, Ag halides, Ag thiosulfates
As	Metal arsenides and arsenates, sulfide ores (arsenopyrite), arsenolite (As ₂ O ₃), volcanic gases, geothermal springs	Pyrometallurgical industry, spoil heaps and tailings, smelting, wood preserving, fossil fuel combustion, poultry manure, pesticides, landfills	As oxides (oxyanions), organo-metallic forms, H ₂ AsO ₃ CH ₃ (methylarsinic acid), (CH ₃) ₂ -AsO ₂ H (dimethylarsinic acid)
Be	Beryl (Be ₃ Al ₂ Si ₆ O ₁₈), phenakite (Be ₂ SiO ₄)	Nuclear industry, electronic industry	Be alloys, Be metal, Be(OH) ₂
Cd	Zinc carbonate and sulfide ores, copper carbonate and sulfide	Mining and smelting, metal finishing, plastic industry, microelectronics, battery manufacture, landfills and refuse disposal, phosphate fertilizer, sewage sludge, metal scrapheaps	Cd ²⁺ ions, Cd halides and oxides, Cd–CN complexes, Cd(OH) ₂ sludge
Cr	Chromite (FeCr ₂ O ₄), eskolaite (Cr ₂ O ₃)	Metal finishing, plastic industry, wood treatment refineries, pyrometallurgical industry, landfills, scrapheaps	Cr metal, Cr oxides (oxyanions), Cr ³⁺ complexes with organic/inorganic ligands
Cu	Native metal (Cu), chalcocite (Cu ₂ S), chalcopyrite (CuFeS ₂),	Mining and smelting, metal finishing, microelectronics, wood treatment, refuse disposal and landfills, pyrometallurgical industry, swine manure, pesticides, scrapheaps, mine drainage	Cu metal, Cu oxides, Cu humic complexes, alloys, Cu ions
Hg	Native metal (Hg), cinnabar (HgS), degassed from Earth's crust and oceans	Mining and smelting, electrolysis industry, plastic industry, refuse disposal/landfills, paper/pulp industry, fungicides	Organo-Hg complexes, Hg halides and oxides, Hg ²⁺ , (Hg ₂) ²⁺ , Hg ⁰
Ni	Ferromagnesian minerals, ferrous sulfide ores, pentlandite	Iron and steel industry, mining and smelting, metal finishing, microelectronics, battery manufacture	Ni metal, Ni ²⁺ ions, Ni amines, alloys
Pb	Galena (PbS)	Mining and smelting, iron and steel industry, refineries, paint industry, automobile exhaust, plumbing, battery manufacture, sewage sludge, refuse disposal/landfills, pesticides, scrapheaps	Pb metal, Pb oxides and carbonates, Pb–metal–oxyanion complexes
Sb	Stibnite (Sb ₂ S ₃), geothermal springs	Microelectronics, pyrometallurgical industry, smelting mine drainage	Sb ³⁺ ions, Sb oxides and halides
Se	Free element (Se), ferroselite (FeSe ₂), uranium deposits, black shales, chalcopyrite–pentlandite–pyrrhotite deposits	Smelting, fossil fuel combustion, irrigation waters	Se oxides (oxyanions), Se-organic complexes
Tl	Copper, lead, silver residues	Pyrometallurgical industry, microelectronics, cement industry	Tl halides, Tl–CN complexes
Zn	Sphalerite (ZnS), willemite (Zn ₂ SiO ₄), smithsonite (ZnCO ₃)	Mining and smelting, metal finishing, textile, microelectronics, refuse disposal and landfills, pyrometallurgical industry, sewage sludge, pesticides, scrapheaps	Zn metal, Zn ²⁺ ions, Zn oxides and carbonates, alloys

Source: Adriano (2001); mineral nomenclature after Mandarino and Back (2004).

ative and invariant with respect to pH in the case of constant-charge clay minerals such as montmorillonite and vermiculite. The constant charge results from ionic substitution in the clay structure (in the past referred to as isomorphic substitution). The surface charge can also be variable, becoming more negative with increased pH as surface functional groups on clay minerals, metal oxides and oxyhydroxides, and organic matter deprotonate. Surface charge can also become more positive as pH decreases as surface functional groups protonate. Clay minerals such as kaolinite and Al-

and Fe-oxides are considered variable-charge minerals (Sparks 2002).

Both physical and chemical forces are involved in adsorption of solutes from solution. Physical forces include van der Waals forces (e.g. partitioning) and electrostatic outer-sphere complexes (e.g. ion exchange). Chemical forces result from short-range interactions, which include inner-sphere complexation involving a ligand exchange mechanism, covalent bonding, and hydrogen bonding (Stumm 1992; Sparks 2002).

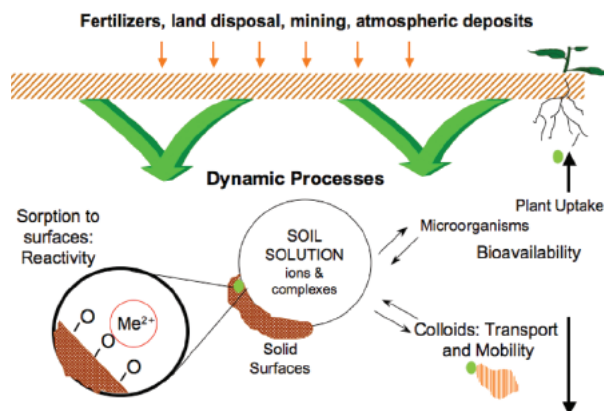


FIGURE 1 Biogeochemical pathways and processes of metals in the critical zone. Me = metal. Tiny green blobs = metal ion; brown blobs = soil particles; orange blob = colloid.

MOLECULAR-SCALE ASSESSMENT OF METAL SORPTION ON NATURAL SURFACES

Until recently, most studies on metal sorption on natural sorbents have been macroscopic and have investigated the role that various environmental effects, such as solution pH, metal/anion concentration, background electrolyte, and time, have on sorption. Over the past decade or more, in situ (under natural conditions where water is present) molecular-scale analytical techniques such as X-ray-absorption fine-structure spectroscopy (XAFS) and attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy have been employed extensively to determine the type of metal surface complexes and products that form on minerals and humic substances (see studies reported in Brown and Parks 2001; Brown and Sturchio 2002; Sparks 2005). Environmental factors, such as pH, surface loading, ionic strength, type of sorbent, and time, affect the type of sorption complex or product. Based on macroscopic and molecular-scale studies, one can predict that alkaline earth cations, Mg^{2+} , Ca^{2+} , Sr^{2+} , and Ba^{2+} , primarily form outer-sphere complexes, while the divalent first-row transition metal cations, Mn^{2+} , Fe^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} , and Zn^{2+} , and the divalent heavy metal cations, such as Cd^{2+} , Hg^{2+} , and Pb^{2+} , primarily form inner-sphere complexes (Sparks 2002, 2005). However, a number of scientists have shown that, at higher metal loadings and pHs, multinuclear metal hydroxide complexes and surface precipitates involving Co^{2+} , Cr^{3+} ,

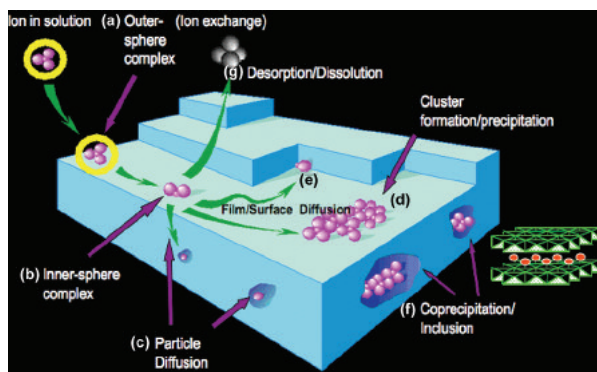


FIGURE 2 Various mechanisms of sorption of an ion at the mineral-water interface: (a) adsorption of an ion via formation of an outer-sphere complex; (b) loss of hydration water and formation of an inner-sphere complex; (c) diffusion and isomorphic substitution within the mineral structure (d); rapid lateral diffusion and formation of a surface polymer or (e) adsorption on a ledge (which maximizes the number of bonds to the atom); (f) upon particle growth, surface polymers end up embedded in the structure; finally, (g) the adsorbed ion can diffuse back in solution, either as a result of dynamic equilibrium or as a product of surface redox reactions. From Charlet and Manceau (1993), with permission.

Cu^{2+} , Ni^{2+} , and Pb^{2+} can form on metal oxides, phyllosilicates, soil clays, and soils (see references in Brown and Parks 2001; Brown and Sturchio 2002; Sparks 2005). Thus, there is often a continuum between surface complexation (adsorption) and surface precipitation. At low-surface coverages, surface complexation (e.g. outer- and inner-sphere adsorption) tends to dominate. As surface loadings increase, nucleation occurs and results in the formation of distinct entities or aggregates on the surface. As surface loadings increase further, surface precipitation becomes the dominant mechanism (Sparks 2002).

RESEARCH FRONTIERS

Particle surfaces, which range in size from nanometers to micrometers, play a profound role in controlling the cycling of toxic metals in the environment. The use of molecular-scale techniques, particularly those that employ synchrotron radiation, have significantly advanced our understanding of metal-surface interactions. Accordingly, the applications of these cutting-edge tools are prominently featured in several of the articles in this issue.

In their article, **Hochella and Madden** introduce the importance of nanoparticles in the cycling of metals. Most of the total surface area in the near-surface region of the Earth is associated with very small particles, and nanoparticles have the largest surface area per unit mass of all particulate matter. The small size and large surface area dramatically affect geochemical reactions. For example, Madden and Hochella (2005) found that Mn^{2+} oxidation reaction rates (the reaction rate was surface-area normalized) are up to two orders of magnitude faster on hematite nanoparticles with grain diameters of 7 nm than those with grain diameters of 40 nm. Another important way in which nanoparticles can affect metal cycling in the environment is through wind-blown dust nanoparticles. *Utsunomiya* (2004) showed that As, Cr, Pb, and Se are associated with airborne nanoparticles. This could pose a serious human health risk since the solubility and reactivity of the metals, due to the small size of the particles, could be enhanced if the particles were ingested into lung tissue (Hochella 2002).

Kretzschmar and Schäfer discuss the role that mobile colloidal particles play in the fate and transport of metals in soils and waters. The particles range in size from 1 nm (i.e. a nanoparticle) to 1 micron and are composed of clay minerals and mineral precipitate phases (Fe, Al, Mn, or Si oxides and hydroxides, carbonates, and phosphates), humic and fulvic acids, and biocolloids (viruses, bacteria, and protozoans).

With the advent of third-generation synchrotron light sources, which provide more intense X-rays and greater spatial resolution, scientists are able to determine the forms and distributions of metals in heterogeneous systems such as soils and plants and mineral-microbe-metal interactions. **McNear et al.** discuss the use of synchrotron-based micro-focused XAFS, X-ray fluorescence spectroscopy and microtomography to speciate metals in heterogeneous soils and plants that accumulate large quantities of metals (hyperaccumulators). **Kemner et al.** employ synchrotron-based techniques to study mineral-microbe-metal interactions and effects on metal chemistry. **Villalobos et al.** discuss trace metal sorption on biogenic Mn oxides that form due to enzymatic catalysis by bacteria and fungi via oxidation of Mn^{2+} (Tebo et al. 1997).

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TABLE 2

PROPERTIES OF IMPORTANT CLAY MINERALS AND METAL OXIDE AND OXYHYDROXIDE SORBENTS IN NATURAL SYSTEMS

Mineral	Chemical Formula	Specific Surface Area (m ² g ⁻¹)
CLAY MINERALS AND OTHER LAYER SILICATES		
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	7-30
Halloysite	Al ₂ Si ₂ O ₅ (OH) ₄	10-45
Pyrophyllite	Al ₂ Si ₄ O ₁₀ (OH) ₂	65-80
Talc	Mg ₃ Si ₄ O ₁₀ (OH) ₂	65-80
Montmorillonite	(Na,Ca) _{0.3} (Al,Mg) ₂ Si ₄ O ₁₀ (OH) ₂ •nH ₂ O	600-800
Diocahedral vermiculite	(K,Na,Ca) _{0.7} (Al,Mg,Fe) ₂ (Si,Al) ₄ O ₁₀ (OH) ₂ •nH ₂ O	50-800
Triocahedral vermiculite	Mg _{0.7} Mg ₃ (SiAl) ₄ O ₁₀ (OH) ₂ •nH ₂ O	600-800
Muscovite	KAl ₂ Al Si ₃ O ₁₀ (OH) ₂	60-100
Minerals of the biotite series	K(Mg,Fe,Al) ₃ (Si,Al) ₄ O ₁₀ (OH,F) ₂	40-100
Minerals of the chlorite group	[(Mg,Al,Li) ₂₋₃ OH ₆](Al,Mg,Li) ₂₋₃ (SiAl) ₄ O ₁₀ (OH,F) ₂	25-150
Allophane	Variable (amorphous hydrous aluminosilicates with a molar Si/Al ratio of 1.2 to 1:1)	100-800
METAL OXIDES AND OXYHYDROXIDES		
Aluminum oxides and oxyhydroxides		100-220
Bayerite	α-Al(OH) ₃	
Böhmite	γ-AlO(OH)	
Corundum	α-Al ₂ O ₃	
Diaspore	α-AlO(OH)	
Gibbsite	γ-Al(OH) ₃	
Iron oxides and oxyhydroxides		70-250
Akaganéite	β-Fe ³⁺ (O,OH,Cl) or Fe ₈ (OH,O,Cl) ₁₇	
Ferrihydrite	~ Fe _{4.5} (OH,O) ₁₂	
Feroxyhyte	δ-FeO(OH)	
Goethite	α-FeO(OH)	
Hematite	α-Fe ₂ O ₃	
Lepidocrocite	γ-FeO(OH)	
Maghemite	γ-Fe ₂ O ₃	
Magnetite	Fe ²⁺ Fe ³⁺ ₂ O ₄	
Manganese oxides and oxyhydroxides		5-360
Birnessite	δ-MnO ₂ or (Na,Ca)(Mn ⁴⁺ ,Mn ³⁺) ₄ O ₈ •3H ₂ O	
Manganite	γ-MnO(OH)	
Groutite	α-MnO(OH)	
Pyrolusite	β-MnO ₂	

Source: Sparks (2002).

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Meet the Authors



John Bargar, research scientist at the Stanford Synchrotron Radiation Laboratory since 1996, received his BS in geology and mineralogy from the Ohio State University (1990) and his PhD in geological and environmental sciences from Stanford University (1996). Bargar's main research interests lie in the areas of geomicrobiology, low-temperature aqueous geochemistry, and mineral-water and membrane-water-interface geochemistry. His current research activities focus on the structural chemistry and environmental reactivity of bacteriogenic minerals, with emphasis on elucidating their roles in the biogeochemical cycling of metals in the biosphere. He carries out these investigations under in situ conditions with synchrotron-based scattering and spectroscopy techniques.



Maxim I. Boyanov received a BSc and an MSc degree in physics from the University of Sofia and a PhD in physics from the University of Notre Dame. In 2003, he joined the Molecular Environmental Science Group at Argonne National Laboratory

as a postdoctoral researcher. His PhD work focused on using synchrotron X-ray techniques to study the molecular binding of dissolved metals to organic ligands, both on the surface and in solution. His current research aims at linking the molecular coordination of ferrous iron to its reactivity, which has implications for the biogeochemical cycling of iron and the removal of contaminants from the environment.



Michael F. Hochella Jr. is professor of geochemistry and mineralogy at Virginia Tech (USA). He received his PhD degree from Stanford University in 1981 under Gordon Brown. For the last 20 years, his research has involved mineral surface physics and mineral-water interface geochemistry, and more recently, nanoscience applied to geochemistry and mineralogy, as well as mineral-microbe interactions. All of this work is generally applied to environmental science. He is a former president of the Geochemical Society and is a recipient of the Dana Medal of the Mineralogical Society of America, the Alexander von Humboldt Research Award, and a Senior Fulbright Fellowship.



Shelly D. Kelly received her PhD from the University of Washington in 1999. She is currently an assistant physicist in the Molecular Environmental Science Group of the Environmental Research

Division of Argonne National Laboratory. Kelly has focused her research on the valence state and chemical speciation of contaminants in biogeochemical systems as revealed by synchrotron X-ray techniques with emphasis on extended X-ray absorption fine-structure (EXAFS) spectroscopy. Her recent interests include the interaction of uranyl with calcium and carbonate in solution, the incorporation mechanism of U^{6+} into the crystallographic structure of calcite, and the interaction of U^{6+} with microbial exudates.



Kenneth M. Kemner obtained his PhD in physics at the University of Notre Dame in 1993. From 1993 to 1996 he was an NRC Post-Doctoral Fellow at the Naval Research Laboratory in Washington, DC. In 1996 he joined the Environmental Research

Glossary of terms related to metals and natural surfaces

Lewis acids and bases

Metals can be classified according to their hard and soft characteristics, based on the principle of hard and soft acids and bases (Pearson 1963, 1968).

Lewis acid – an electron pair acceptor. All metal ions or atoms and most cations are Lewis acids and capable of accepting a pair of electrons from a Lewis base (anion). A metal that is a hard Lewis acid has a high positive oxidation state, small size, and low polarizability (e.g. potassium and calcium), while a metal that is a soft Lewis acid has a large size, low positive charge, and high electronegativity (e.g. copper and zinc). Most metals are soft or transition acids, meaning they have low positive charge and large size and form covalent bonds with ligands.

Lewis base – an electron pair donor. A hard Lewis base is an electron donor of low polarizability and high electronegativity (e.g. nitrate and sulfate), while a soft Lewis base is a donor of large size and high polarizability (e.g. iodide and cyanide) (Pearson 1963, 1968; Morris 1992; Sparks 2002).

Sorption terminology

Adsorption – the accumulation of a substance or material at the interface between a solid surface and a bathing solution.

Inner-sphere surface complex – no water molecule is present between the ion or molecule and the surface functional group to which it is bound, and the bonding is covalent or ionic. Inner-sphere complexes can be monodentate (metal is bonded to only one oxygen) or bidentate (metal is bonded to two oxygens) and mononuclear or binuclear. Inner-sphere complexation can increase, reduce, neutralize, or reverse the charge on the sorptive regardless of the original charge. Adsorption of ions via inner-sphere complexation can occur on a surface regardless of the original charge. Inner-sphere complexation is usually slower than outer-sphere complexation and is often not reversible. **Outer-sphere surface complex** – a water molecule is present between the surface functional group and the bound ion or molecule (Sposito 1989). Outer-sphere complexes

involve electrostatic coulombic interactions. Outer-sphere complexation is usually a rapid process that is reversible, and adsorption occurs only on surfaces that are of opposite charge to the adsorbate.

Polymerization – the formation of small multinuclear inorganic species such as dimers or trimers on a surface.

Sorption – a general term that is used when the retention mechanism at a surface is unknown. Adsorption, surface precipitation, and polymerization are all examples of sorption.

Surface complex – the interaction of a surface functional group with an ion or molecule present in the soil solution can create a stable molecular entity called a surface complex. The overall reaction is referred to as surface complexation.

Surface functional group – a “chemically reactive molecular unit attached at the boundary of a solid with the reactive groups of the unit exposed to the soil solution” (Sposito 1984). Surface functional groups can be organic or inorganic molecular units. Organic functional groups are associated with humic substances

(naturally occurring heterogeneous organic substances of high molecular weight and of brown to black color, i.e., humic and fulvic acids, and humin). The major organic functional groups are carboxyl [$R-C(=O)(-OH)$, where R is an aliphatic backbone] and phenolic (Ar-OH, where Ar is an aromatic ring) (Stevenson 1982; Sparks 2002). The major inorganic surface functional groups in soils are (1) the siloxane surface associated with the plane of oxygen atoms bound to the silica tetrahedral layer of a phyllosilicate (clay mineral) and (2) hydroxyl groups associated with the edges of inorganic minerals such as kaolinite, amorphous materials, and metal oxides and oxyhydroxides. Surface functional groups on metal oxide and oxyhydroxide, clay mineral, and organic matter surfaces play a significant role in metal sorption processes.

Surface precipitation – the formation of a three-dimensional phase product on a surface.

Division at Argonne National Laboratory near Chicago, Illinois where he formed the Molecular Environmental Science Research Group, an integrated multidisciplinary research group making use of third-generation synchrotron radiation for environmental research. Since 1997 he has been investigating mineral–microbe–metal interactions and their role in affecting the mobility of contaminant metals and radionuclides. In 1999 he received the Presidential Early Career Scientist Award and the DOE-Office of Science Early Career Scientist Award. In 2000 he received the International Union of Crystallography Young Scientist Award.



Ruben Kretzschmar is professor of soil chemistry in the Department of Environmental Sciences at the Swiss Federal Institute of Technology (ETH) in Zurich. He received his PhD in soil chemistry from

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Andrew Madden received his BS degree in geology at Michigan State University and his PhD at Virginia Tech where he worked with Mike Hochella in the NanoGeoscience and

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David McNear received his BS and MS degrees from the Pennsylvania State University and currently is a graduate fellow with Dr. Donald Sparks at the University of Delaware. His research

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Edward O'Loughlin is a staff scientist in the Environmental Research Division at Argonne National Laboratory. He received his Bachelor's degree in biology from

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Thorsten Schäfer is Head of the Colloid Chemistry Group since 1999 and Head of the Radionuclide Migration Group since 2004 at the Institut für Nukleare

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Donald L. Sparks is S. Hallock du Pont Endowed Chair of Soil and Environmental Chemistry at the University of Delaware. His research

focuses on the kinetics of soil chemical reactions and the surface chemistry of soils. He and his group have been leaders in employing synchrotron-based techniques to study metal, metalloid, and nutrient reactions in soil minerals, soils, and biosolids. He has advised and mentored 60 graduate students and

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Ryan Tappero is a PhD student in environmental soil chemistry (University of Delaware). He studied geology at Sierra College and earned his BS in soil science and MS in soil chemistry from California

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Mario Villalobos has an undergraduate degree in chemistry from UNAM in Mexico, where he currently holds a full-time researcher position; a Master's degree in soil chemistry from Wageningen Agricultural

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