MERG Report 2000-6

Possible Mechanisms of Natural Attenuation of Metal-Bearing Waters in Soils in Northern Climates

By Dylan MacGregor

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prepared for

Mining Environment Research Group

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March 2000

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1. INTRODUCTION

Mining of metallic ores exposes metal-bearing minerals in wall rock, tailings and waste rock to accelerated rates of weathering; this can lead to increased metal loading to the environment. Waters draining natural exposures of metalliferous rocks and rocks exposed through mining or mineral exploration commonly contain high concentrations of metals. The aquatic environment downstream from these sites can be negatively impacted by the resulting high metal flux. Natural processes that act to reduce metal concentrations in these waters help to mitigate the effects of water-borne metals on the receiving environment. A number of natural soil processes can act to remove metal species from metal-bearing water; in many situations, metal-bearing waters flow through soil before joining a surface water body, in which case soil processes may reduce metal loading to downstream aquatic communities. These processes can be important at a number of sites: at the base of waste rock dumps, where uncontrolled drainage seeps into the subsurface; at the mouths of adits discharging metalliferous waters which then seep into the ground; down gradient of tailings dams, where metal-bearing seepage flows through soils; at active or abandoned exploration sites, where waters draining recent exposures of metalliferous rocks percolate into the subsurface; at natural metalliferous rock exposures, where drainage waters subsequently flow through the soil; and, on the perimeter of stream channels, where metal-bearing waters contact or flow through soils. The northern climate influences soil properties, geochemical processes and the ways in which water-borne metals move through soils. The presence of permafrost impacts site hydrology on a spatial and on a seasonal basis, and permafrost processes have potential implications for metal behaviour in soils.

For natural attenuation processes to mitigate the effects of increased rates of metallic mineral weathering on the environment, it is necessary that metals removed from metalliferous waters be stored in a form that is stable over the range of conditions which exist at the attenuating site. Long term storage of metals is essential for natural attenuation processes to be of any practical value. Short term storage (e.g. seasonal retention) may result in periods of metal accumulation followed by large metal fluxes to the receiving environment over a short time period resulting from changes in site conditions (e.g. seasonal changes such as high spring flows). Understanding the temporal stability of different forms of metal storage and the processes by which natural attenuation in soils occurs will allow more accurate estimates of metal fluxes to the receiving environment at the types of sites mentioned above. This knowledge may also prove beneficial in the design of passive water treatment systems for northern mines and exploration sites. The following is a literature review of the current state of knowledge regarding possible mechanisms for natural attenuation of metal-bearing waters in northern soils.

2. METAL SPECIES IN NATURAL WATERS

The attenuation of metal-bearing waters by soils is in part governed by the different hydrogeochemical species present. Typically, waters impacted by the oxidation of sulphide minerals are rich in iron and contain variable amounts of SO_4^{2-}, CO_3^{2-}, HCO_3^-, OH^- and H^+ ions, possibly accompanied by dissolved organic species, in addition to metals (Herbert, 1994; Kimball et al., 1994). Metals are transported as dissolved cations, as dissolved complexes with the above species or in association with organic or inorganic particulate matter (Gunn et al., 1988; Gallacher and Pulford, 1989). Attenuation in soil occurs when metal cations or complexes bind chemically to the soil substrate, when an insoluble phase precipitates or when filtration removes particulate matter from water. Of the metal species commonly of concern, zinc and cadmium are among the most mobile (Miller, 1978) and thus resist attenuation to a greater degree than other metals.

3. NATURE OF NORTHERN SOILS AND SOIL PROCESSES

3.1 Composition

Soils consist of mineral and organic matter. Organic matter is classified according to the degree of degradation it has undergone. In general, refractory organic material (that most resistant to degradation) has the highest capacity for binding with dissolved cations (Sparks, 1995). The mineral constituents of soils consist of rock fragments, primary and secondary (weathering) minerals and amorphous solids. Of the primary phases, the clay minerals are the most important in terms of metal attenuation. Clay minerals tend to have mineral-specific net negative surface charges and cations, particularly metals, are electrostatically attracted to these surfaces (Figure 1). Clay mineralogy thus influences attenuation capacity, as the mass of metal which can be electrostatically bound to a unit mass of clay differs for each clay mineral. Furthermore, clay minerals have a high specific surface area (large surface area per unit mass of soil) and thus provide large areas of reactive surface on which binding of metal cations can occur (Yong et al., 1992).

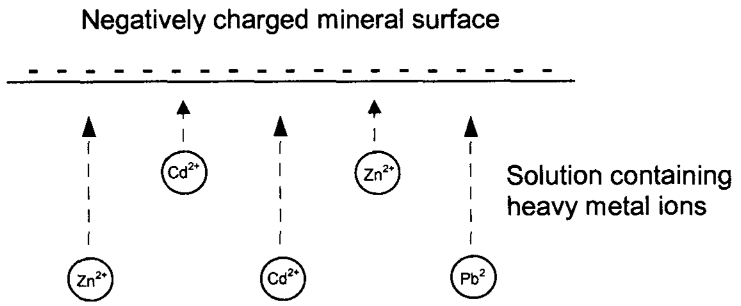

Figure 1. Positively charged heavy metal cations in solution are electrostatically attracted to the negatively-charged surface of clay minerals.

Additional compositional control on attenuation of metals is exerted by secondary minerals such as metal oxides and hydroxides in soils. These tend to have high specific surface areas and readily form from dissolved metal species under oxidizing surface conditions at pH levels greater than 3 (Yariv and Cross, 1979). Both manganese and iron oxides, hydroxides and oxyhydroxides are well known to precipitate from mine drainage waters and to have high levels of substitution of heavy metal cations for other metal ions within their respective crystal lattices (Gong and Donahoe 1997; Lin and Herbert, 1997; Randall et al., 1999). Processes associated with freezing can promote the formation of metal oxyhydroxides (Makarov, 1988); Lehman et al. (1999) found that, in a test of several inorganic compounds, a granulated iron oxyhydroxide produced by crystallization through freezing removed the most metals from a dilute aqueous solution. This evidence suggests that the freezing-induced precipitation process can result in a mineral structure that has a high capacity for removing metals from contaminated waters.

3.2 Organic matter

Northern soils are typically immature, having a poorly developed soil profile whose characteristics are dominated by parent materials, weathering and physical processes (Dobrovolskiy, 1996). The northern climate inhibits the breakdown of plant residues; thick accumulations of organic material in various states of decomposition are common at the surface of northern soils (Chague-Goff and Fyfe, 1997). On slopes, where solifluction causes soil mixing with downslope movement, organic material can become distributed vertically throughout the soil. Freeze-thaw processes such as cryoturbation also facilitate the mixing of organic matter to some depth within the soil. Where permafrost is present, the permafrost table acts as a barrier to vertical movement of water and dissolved constituents; organic matter can be transported vertically in solution and be subsequently deposited near the permafrost table (Brown et al., 1981). This can result in the development of an organic rich horizon near the base of the active layer. These processes which facilitate the vertical mixing of organic matter are important in the context of subsurface attenuation of water-borne metals. Organic-rich horizons and vertically mixed organics can greatly increase a soil's ability to complex with dissolved cations. Decomposition is not a prerequisite; studies of metal complexation with Sphagnum moss have shown that living and dead Sphagnum have equal capacities for removing metals from solution (Shotyk, 1984), indicating that the uptake processes are strictly chemical and not biologically mediated.

3.3 Grain size distribution

The coarse fraction of soils has very low specific surface area and as such is essentially inert from a physico-chemical standpoint. Soils dominated by sands and gravels will have low attenuation capacities. In general, as the proportion of clays in a soil increases, the attenuation capacity will increase (Yong et al., 1992). However, metal species in solution need access to reactive clay surfaces to be removed from the water; if the soil has a very low permeability, the rate of cation supply to the negative clay surfaces may limit the amount of attenuation which can occur. A soil capable of removing a maximum mass of metal from solution would contain significant clay and/or organic material while at the same time containing sufficient coarse material to allow metal-bearing waters to move freely through the soil (Benner et al., 1997).

3.4 Permafrost processes

Where permafrost is present, metal and water movement is largely restricted to surface water bodies and, during summer, to the unfrozen zone (the active layer) extending from the ground surface to the depth of annual thaw (the permafrost table- Figure 2). Permafrost processes operating within the active layer can act to remove metals from solution directly as well as to enhance metal attenuation by standard mechanisms.

3.4.1 Freezing processes

As freezing of water proceeds, impurities such as particulate and dissolved species are excluded from the highly ordered ice crystal structure. Removal of water from solution in this manner concentrates the excluded material in the remaining solution (Corte, 1962; Watterson, 1985; Makarov, 1988). Freezing in soils begins at the ground surface and proceeds downwards (Figure 2); this has the effect of concentrating solutes and particulate matter in an unfrozen zone between the freezing front and the permafrost table (Makarov, 1988; Outcalt and Hinkel, 1996). Chodak (1988) reports accumulation of iron compounds, clay minerals and organic matter at the base of the active layer via this process.

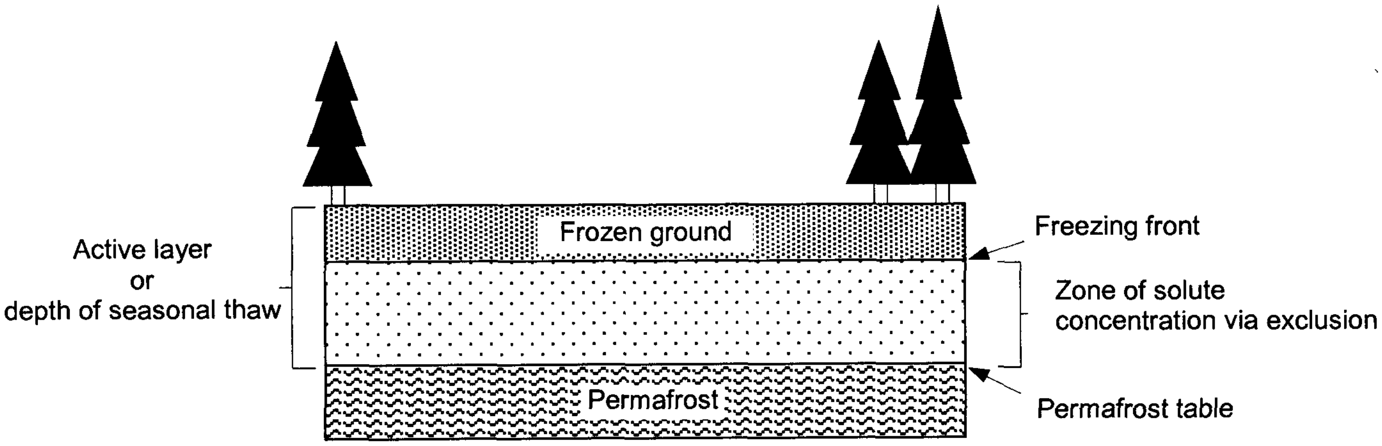

Figure 2. Schematic diagram illustrating penetration of freezing front into the ground and the zone where solute concentrations are increased through solute exclusion during ice formation.

Ice formation in soils begins not on the surface of soil particles but in interparticle fluid and proceeds with decreasing temperature to remove greater amounts of water from the bulk solution (Anderson, 1968). When freezing ceases, soil particles remain separated from ice by an unfrozen layer of solute-rich water. The thickness of this liquid layer is controlled by temperature, varying from 50 Å at 0° C to being completely frozen at -80° C (Anderson, 1968); the liquid nature of this film allows movement of water and impurities through frozen soils under all conceivably realistic soil temperature regimes.

3.4.2 Electrical potential

Although freezing water tends to exclude impurities, some dissolved and particulate species are inevitably incorporated into the structure of ice. During ice formation, more anions than cations are included into the ice crystal structure; this establishes a measurable charge distribution, or electrical potential, across the solid/liquid interface (Watterson, 1985). The magnitude of this electrical potential varies, largely depending on the ionic strength of the unfrozen solution, and is commonly reported to be on the order of 0.2 V (Romanov, 1988; Parameswaran and Mackay, 1996). Although the precise nature of metal-soil interactions in the presence of this electrical potential is poorly understood, there is evidence that it facilitates removal of metals from solution; Watterson (1985) describes the precipitation of elemental gold from natural stream waters through repeated freezing and thawing.

3.4.3 Water, solute and particulate migration

During the initial stages of freezing as the freezing front moves towards the permafrost table, exclusion of solutes and particulates at the freezing front set up concentration gradients which cause diffusion-driven downward migration of metals, organics and particulate matter (Watterson, 1985; Chodak, 1988; Hinkel et al., 1997). Following the initial freezing phase, diffusion of ions from the concentrated region at the base of the active layer occurs both down into the permafrost (Makarov,1988) and up towards the ground surface (Cary and Mayland, 1972; Outcalt and Hinkel, 1996). Makarov (1988) reports diffusion of metals derived from mining activity to depths of 5 to 9 m below the permafrost table in northeast Asia; similarly, elevated elemental concentrations below the permafrost table were noted in western NWT (Chague-Goff and Fyfe, 1997). Gaseous water losses to the atmosphere via sublimation of frozen water and evaporation of unfrozen films occur at the soil surface during the winter months; this results in movement of solute-rich waters from depth under tension via capillary forces towards the ground surface (Cary and Mayland, 1972). Continued water losses can lead to the formation of highly soluble efflorescent minerals from solute species, including metals, at the ground surface (Miller, 1978; Makarov, 1988; Outcalt and Hinkel, 1996) which attest to the occurrence of ionic migration.

4. MECHANISMS OF NATURAL ATTENUATION

A number of different processes are capable of removing dissolved and particulate metals from metal-bearing waters. These include precipitation, coprecipitation, adsorption and organic complexation and ligand exchange; each is affected in some way by northern environmental conditions.

4.1 Precipitation

Removal of metals from solution via precipitation requires saturation of the solution with respect to the metal species. Saturation of solution can occur when freezing of solution is active or through evaporation. Ice crystal growth in solution proceeds by the orderly addition of water molecules to the crystal structure of ice; during this process, any impurities such as dissolved species or particulates in solution are excluded from the ice and concentrated in the remaining solution. Assuming component species are available, mineral precipitation can occur when the concentration of component species in the remaining solution exceeds the mineral's solubility (Anisimova, 1988). Kwong et al. (1994) note the formation of hydrozincite ($Zn_5(CO_3)_2(OH)_6$) in small streams in the Keno Hill district, central Yukon, by "cryogenic precipitation".

Precipitation is effective for the long-term storage of metals only if the precipitates are stable under the range of prevalent environmental conditions. If exclusion during freezing or concentration through dehydration results in the formation of highly soluble mineral salts, these will readily dissociate on future contact with water. Where significant metal isolation occurs via the formation of soluble salts, there is a high likelihood of having a subsequent precipitation or snowmelt event remobilize large quantities of metals and deliver these metals to the receiving environment. At Iron Mountain, California, formation of soluble metal sulphates and their subsequent dissolution during peak flow events results in arguably the worst case of mine-generated contamination in the world (Nordstrom and Alpers, 1999). Under anoxic conditions, precipitation of sulphide minerals can be an effective mechanism for metal attenuation, provided that reducing conditions prevail (Krauskopf and Bird, 1995). Certain metal oxides, hydroxides and oxyhydroxides [((oxy)hydr)oxides] form readily under oxygenating conditions and are typically stable. However, a shift to reducing conditions or a dramatic decrease in pH result in ((oxy)hydr)oxide dissolution. Certain metal carbonates, particularly cerussite ($PbCO_3$), readily form (Bloom, 1987) and are stable even under mildly acidic conditions (Kwong et al., 1994). Metal carbonate species play an important role in the attenuation of some metals under near neutral or basic conditions. For metals such as zinc and cadmium, however, the solubilities of the carbonate minerals are sufficiently high that even under slightly alkaline conditions, little attenuation is likely (Bloom, 1987).

4.2 Coprecipitation

As a mechanism of metal attenuation in soils, coprecipitation can be very important. It involves the incorporation of heavy metal species into the crystal structure of a forming mineral through substitution or into an existing mineral by diffusion (Krauskopf and Bird, 1995). Metal attenuation via coprecipitation is largely concerned with the oxides, hydroxides and oxyhydroxides of iron and manganese (Yariv and Cross, 1979). These generally have high specific surface areas which facilitate diffusive attenuation of dissolved cations and commonly form surface coatings on soil particles, minerals and rocks (Bertsch and Seaman, 1999); they form the typical red staining associated with waters draining sulphide weathering sites. Manganese and iron precipitates often form from waters influenced by sulphide oxidation (Webster et al., 1994) and are thus able to remove other metals of concern from the same waters. Manganese and iron precipitates are known to have formed cryogenically in the active layer in permafrost soils impacted by mine drainage (Makarov, 1988); removal of other metals via coprecipitation within the active layer likely reduces off-site metal loading to the environment. Some evidence suggests that cryogenic ferric hydroxides have a structure which enhances their capacity to remove metals from solution (Lehman et al., 1999). Cameron (1977) found that copper and arsenic coprecipitated with iron oxides in permafrost soils in central NWT. In moderately acidic environments, manganese and iron precipitates constitute the most important geochemical control on metal mobility, as these minerals are typically stable down to a pH of around 3 (Doyle, 1972; Herbert, 1995; Lin and Herbert, 1999). The heavy metal affinity of manganese and iron precipitates makes these minerals critical sinks for metals in neutral environments as well; Boyle (1965) notes high zinc, lead and silver values in manganese precipitates in neutral streams in central Yukon.

4.3 Adsorption

The various processes encapsulated by the term adsorption consist of interactions at a solid/liquid interface between a charged mineral or colloid surface and an oppositely charged species in the liquid (Yariv and Cross, 1979). In the case of a dissolved heavy metal cation, the absorbing surface would be negatively charged, such as is characteristic of the clay minerals. Adsorption of heavy metal cations in soils generally occurs on clay mineral surfaces, as well as on organic matter, amorphous inorganic materials and metal ((oxy)hydr)oxide precipitates (Sparks, 1995). The electrostatic attraction between the anionic surface and the cationic species in solution partially determines the strength and nature of the interaction; other controlling factors are pH, initial adsorbed species and cation concentration in solution (Krauskopf and Bird, 1995).

At mildly acidic to neutral pH, the degree of adsorption of a cationic species depends largely on the concentration of that species in solution- high cation concentrations result in high removals from solution via displacement of existing adsorbed species. In permafrost soils exposed to heavy metal-bearing waters, cation concentrations at the base of the active layer can be greatly elevated during periods of downward freezing. These high concentrations can lead to significant masses of metal being removed from the water. Adsorbed metal is stable barring a dramatic decrease in pH- high levels of acidity result in H^+ ions displacing metal cations at adsorption sites on negative surfaces of soil constituents.

4.4 Organic complexation and ligand exchange

Metal-organic matter interactions in soils are complex processes which are poorly understood at present. Interactions take the form of electrostatic bonding, complexation (involving one or more bonds between a metal ion and a functional group or groups on the organic surface) or ligand exchange (in which a metal ion or complex displaces a functional group with similar characteristics from the organic surface) (Sparks, 1995). Efficiency in metal retention by organic matter depends on pH, metal concentration and the amount of organic matter available (Schnitzer, 1984), with efficiency being highest for low metal concentrations, neutral pH and high proportions of organic matter.

Low rates of microbial breakdown of organic matter result in northern soils typically having high organic matter contents. This organic matter can be mixed vertically by cryoturbation at sites of low relief and by solifluction at steep sites; this mixing permits the organic matter to contact a larger proportion of the groundwater flow than otherwise and likely can lead to higher removal of water-borne metals. Where organic matter has accumulated at the permafrost table by exclusion and downward migration, elevated removals of metal from groundwater are also possible (Chodak, 1988). Finally, Watterson (1985) states that the electrical potential generated during freezing facilitates the formation of metal-organic complexes; this electrical effect would also increase metal uptake from soil solution.

5. DISCUSSION

Elevated metal concentrations are a common characteristic of waters draining metalliferous rocks. Exploration and mining increase the exposed surface area of material with high metal content; subsequent leaching of this material through precipitation, snowmelt or contact with ground- or surface waters can increase the quantity of metals entering natural waters.

Waters leaching metal-bearing rocks often drain through shallow soils prior to entering a surface water body. Metal attenuation mechanisms operating within the soil column will limit the quantity of metals transported to surface waters. The northern climate causes repeated freezing and thawing of the soil surface; during freezing, solutes and impurities are excluded from the ice and are concentrated in the water beneath the freezing front. This concentration increases the likelihood of metal species interacting with soil constituents and being removed from soil fluid. If the metal-soil 'bond' is stable under the range of conditions that occur at a site, it is reasonable to expect that the soil will act as a long-term sink for metals. Diffusion of metals into underlying permafrost beneath the permafrost table will also result in long-term storage, as permafrost is relatively impermeable and leaching of metals from below the permafrost table would be low.

Site-specific evaluation of a soil's attenuation capacity is necessary if knowledge of aqueous metal transport through soils is required. The stability of retained metal species over a range of likely site environmental conditions should be considered during evaluation; if a retained metal species is mobilised under a likely change in site conditions, retention may result in short-term storage only. Long-term stability is critical if a soil is to provide a measure of environmental protection against aqueous heavy metal contamination.

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ISBN 1-55018-985-9