

Soil Microorganism-mineral-organic Matter Interactions and the Impact on Metal Mobility

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Soils are huge reservoirs of micro-organisms. They contain all the main groups of microorganisms with a very large diversity of bacteria, fungi, algae, protozoa. In the upper layers of soils, bacteria can have a biomass of 1,000 to 4,000 kg·ha⁻¹ and an average number of 10⁶ to 10⁹ g⁻¹ of dry soil. Fungi have approximately the same to slightly higher biomass. Both bacteria and fungi are now well recognized as key agents of biogeochemical cycling of major and trace elements and as main actors of soil functioning. Other microorganisms as algae (photosynthetic organisms), present at the soil surface, are not so well known in soils and play a minor role, but are considered as endolithic pioneer organisms involved in rock weathering particularly in cold and warm deserts. Lichens, a symbiotic association between algae and fungi, are also interesting as colonizing organisms and weathering agents.

Soil fungi and the larger part of soil bacteria are chemoorganotroph, living at the expense of organic compounds, but different strategic groups of bacteria are chemolithotroph, living at the expense of inorganic compounds (sulfur oxidizers, iron oxidizers, ammonium oxidizers, ... and CO₂ fixing organisms). In order to generate energy for their growth microorganisms oxidize organic or inorganic materials (electron donors) and reduce for their aerobic or anaerobic respiration and for fermentation processes, inorganic (O₂, NO₃⁻, Mn⁴⁺, Fe³⁺, SO₄²⁻, CO₂) and organic compounds. They also form and release metabolic (acid, complexing, alkaline) compounds. All these energetic, nutritional strategies and metabolic pathways can be directly or indirectly

involved in the solubilisation or insolubilisation of mineral elements, the weathering of minerals, the formation and deposit of minerals and of organo-mineral compounds.

The main microbial processes involved in solubilisation of metals are briefly summarized here after (1) production of acid and/or chelating or complexing compounds able to dissolve and weather silicates, phosphates, carbonates, oxides, sulfides, (2) reduction of iron and manganese involving dissolution of oxides and oxyhydroxides and of associated elements (Al, Ni, Co, Cr, ...), (3) oxydation of sulfides and metal polysulfides bearing metals (Cu, Pb, Ni...), (4) biosorption and bioaccumulation of many metals (uptake from solutions or from solid phases), (5) direct or indirect oxydation (e.g. U, Cr, Hg) or reduction (e.g. Ra) of different elements.

Microbial insolubilisation of metals can involve different types of reactions (1) biodegradation of organic ligands releasing a chelated or complexed metals, (2) formation of hydroxides and oxyhydroxides of iron and manganese acting as sinks for metals, (3) sulfate reduction and deposit of metal sulfides (e.g. Ni, Pb, Cu,...), (4) bioaccumulation, biosorption processes independently and in excess of the nutrient requirements (many metals are concerned).

Some general mechanisms concern processes involving changes in speciation of metals by dissolution of parent materials, by reduction or oxydation or acidification of their environments. At the opposite specific mechanisms occurred such as methylation processes and volatilization of elements

(Pb, Sn, Sb).

All these processes depend on biological, physical and chemical environmental parameters: availability of organic and inorganic energy sources (electron donors and acceptors) and nutrient conditions (e.g. deficiency in nutrients such as iron, nitrogen...) for the microorganisms, adaptability and activity of microbial communities, crystallochemistry and surface properties of minerals, particle size of minerals, humidity, temperature... They occur in all the types of soils, both in rhizosphere and non rhizosphere soils. Depending on the processes involved, the interactions at the surface of the minerals e.g. contact or not contact with the mineral surfaces are of great importance in particular for the oxidation or reduction processes.

To illustrate more accurately the impact of microorganism-mineral-organic matter interactions on the metal mobility, examples are well provided by the biogeochemical cycle of iron and some associated major (Al, Mn) and trace elements (Ni, Co, Cr, ...).

Iron, 4th element of the earth crust and essential micronutrient, occurs in soils, mainly as primary and secondary minerals, originating either from parent material or from their weathering (oxides, silicates, carbonates, sulfides, phosphates), but also as organo-mineral compounds. It is present at low solubility, excepted in acid and or reducing conditions. Iron is consequently more often not or slightly bioavailable. But it has a high reactivity due to its ability to be reduced or oxidized or to form organo-mineral soluble complexes. Its mobility is determined by acid-base and redox conditions and by the presence of organic ligands. Such parameters are not strictly chemically and physico-chemically mediated, but are controlled by microbial activities involving different chemoorganotroph and chemolithotroph communities which permanently determined and modify the biotic and abiotic factors. In fact, soils contain bacterial and fungal communities which by different strategies are involved in iron and metal dissolution and accumulation processes.

In acid and neutral environmental conditions, aerobic or micro-aerophilic autotrophic or mixotrophic bacterial communities oxidize ferrous to ferric iron for their energetic requirements. Iron oxidation is often associated to sulfur and directly or indirectly to metal and non metals dissolution. Surface, crystallo-chemical, electrochemical properties of sulfides are of major interest. Such processes are at the origin of

dissolution of metals (Cu, Ni, U,...) and they end in the formation of ferric deposits as hydroxides or oxyhydroxides associated to other elements excepted in acid or complexing conditions. In strong acid conditions, bioleaching (solubilization, extraction) of metals is dominant.

Other bacterial communities, aero-anaerobic or anaerobic, use ferric iron as electron acceptor in anaerobic respiration or in complement of fermentation. Iron is mobilized (solubilized) as ferrous iron accompanied by other metals present in oxides and oxyhydroxides and can stay in solution in reducing or acidic conditions. Such processes occur not only in waterlogged conditions but also in temporarily hydromorphic soils. They concern soluble forms (ferric chloride, ferric citrate, ...) and insoluble forms of iron (lepidocrocite, goethite, hematite, limonite). The IRB regulation depends on crystallinity, particle size (surface area) substitution in the mineral structure, presence of ligands increasing dissolution, presence of subtle promoting electron transfer (e.g. quinonic compounds such as ADQS), contact between bacteria and mineral... Very significant correlations are observed between IRB activity and soil organic matter (OM) mineralization but with different rates and yields, depending on the availability of organic compounds and of iron and of the biodegradability of OM. These processes are largely spread in different environments. They modify the distribution of iron and of their associated elements (e.g. heavy metals) in the different compartments of the solid phase. They increase their availability and coefficient transfer to the plants.

These iron reducing bacterial (IRB) communities present a very large diversity of bacterial populations as recently observed using molecular biology tools. They have also a large adaptability associated to their diversity. They are strongly involved in the functioning and evolution of soils in temperate, tropical, cold countries and can have beneficial or harmful effects.

Fungi (mycorrhizal and saprophytic) and bacteria synthesize and release complexing agents (e.g. polycarboxylic, hydroxy-carboxylic, phenolic, hydroxamic ... acids) of iron. The rhizospheric bacteria producing such compounds are involved in mineral weathering and the solubilisation of iron and other metals and so promote their transfer to the plant. Some of these complexing agents, the siderophores, having 3 acid hydroxamic functional groups or 3

di-ortho-phenol (catechol) functional groups form very stable organo-metallic complexes involved in dissolution and transfer of ferric iron. Other metals are concerned less specifically. They are very efficient in dissolution of ferric oxides.

All these processes, more or less specifically involved in solubilization and/or deposit of metals, end in the cycling of metals, weathering of minerals, functioning of soils, increase of metals availability in both rhizospheric and non rhizospheric soil sites. They occur in the weathering of different minerals and the behaviour of many elements (iron, aluminium,

trace metals, phosphorus, non metal trace elements, sulphur, arsenic...) and can have beneficial but also harmful effects in the plant - soil systems (e.g. beneficial or toxical effect on rice in paddy fields). The knowledge of the structure and functions of microbial communities involved is in progress but with the parameters controlling their dynamic and activities they need to be better well defined (e.g. availability of organic matter and iron). Basis for models and for environmental biotechnologies are also well progressing.