
Screening the importance of soil micro-organisms on radionuclides mobility

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Abstract. In surface soils, the native physical and chemical properties of the abiotic components control most of the sorption-desorption processes. Moreover, micro-organisms may significantly modify the speciation of trace elements and/or radionuclides and subsequently determine their fate, to a large extent. Micro-organisms, mainly bacteria and fungi, develop many strategies that may affect indirectly or directly the behaviour of trace elements. Due to their activity, changes in the pore-water composition, e.g. pH, redox-potential, may occur in relation with organic acid production or solid phase alteration, reduction or oxidation of metallic oxo-hydroxides, and mineralization of organo-metallic complexes. Micro-organisms may also directly modify the speciation of radionuclides as a result of bio-accumulation in living cells, biosorption on cellular components, direct reduction or oxidation, biomethylation, etc. Each one of these microbial processes may either increase or decrease radionuclide mobility, depending on the element, the soil reactivity and the environmental conditions. The resulting effect of these processes is still poorly known. This literature review intends to present a comprehensive overview of the role of micro-organisms on radionuclide mobility. It aims at classifying these elements, regarding to their potential sensitivity to these microbial processes. It summarizes the theoretical effect of these mechanisms, resulting in a potential increase or decrease of the solid-liquid distribution. The environmental significance of such processes for various biogeochemical radionuclides cycles still remains to be confirmed by experiments. (This study is part of a research program supported by Andra).

1. INTRODUCTION

The general scope of this work was to produce an operational review intended to describe the effect of the soil micro-organisms on the behaviour of various trace elements including radionuclides, and to classify these trace elements regarding the importance of microbial effects on their mobility in surface soils.

The whole investigation relates to the following elements: americium, antimony, arsenic, beryllium, boron, cadmium, caesium, chromium, tin, iodine, nickel, niobium, lead, plutonium, protactinium, radium, selenium, technetium, thorium, uranium. A book has been published [1] including the description of the microbiological mechanisms which control the behaviour of trace elements in the soil – plant system; in addition, bibliographical fact-sheets describe for each element, the characteristics of their behaviour in soils and the modifications induced by the microbial mechanisms on their mobility and bio-availability.

2. MAIN MICROBIAL MECHANISMS INFLUENCING THE MOBILITY OF ELEMENTS

When introduced into the soil, all these elements may possibly undergo physico-chemical transformations according to their own reactivity and speciation and to the physicochemical properties of the soil: temperature, pH, oxydo-reduction potential, concentrations of major and toxic elements,

etc. The intensity and kinetics of mobilization or immobilization processes can be strongly influenced by the direct and/or indirect actions of the micro-organisms. The main microbial mechanisms influencing the mobility of trace elements are reported in table 1.

2.1 Mobility enhancement

The micro-organisms are indirectly involved in element solubilization by alteration of solid components of the soil due to the production of complexing compounds and/or by changes of the redox conditions (O_2 respiration, H_2 production, etc.) [2]. Organic acids and/or complexants are produced by various chemo-organotrophic bacteria and fungi. These metabolites may influence the dissolution of silicates, phosphates, oxides, sulfides, carbonates... by proton exchange and formation of soluble organo-metallic complexes [3]. The dissimilatory reduction of iron, manganese and sulfur may also dissolve the elements associated with oxo-hydroxides: in anaerobic conditions, especially in hydromorphic soils, some bacteria can solubilize Fe^{3+} or Mn^{4+} by direct enzymatic reaction [4] or by fermentation [5, 6]. This is known as a major mechanism occurring in uranium mill tailings for uranium and radium behaviour [7]. Sulfurs or metallic polysulfurs may be oxidized by lithotrophic bacteria, depending on redox and pH conditions. This reaction results in the neo-formation of oxidized phases such as sulfates, oxides, carbonates, etc. Moreover, a concomitant bacterial production of H_2SO_4 may occur, which will enhance the dissolution of many elements, e.g. Cu, Pb, As, Ni, etc. [4, 8].

Another factor that will possibly enhance the elements mobility is their biosorption, followed by the cell death, which will produce colloidal fractions, able to migrate downward by preferential flow. This concerns many elements/radionuclides (Ni, Pb, Cr, Cd) and is specially important for actinides [9, 10].

2.2 Retention or immobilization

Micro-organisms use organic ligands as a source of energy, predominantly in slightly acid and aerobic medium. The biodegradation of the ligand releases the associated elements, which afterwards can precipitate as insoluble metallic hydroxides, as it is observed for cadmium [11].

In aerobic medium, the oxidation of Fe^{2+} et Mn^{2+} by autotrophic and mixotrophic bacteria [12, 13] may favour the retention of trace elements, through non-specific formation of substituted oxo-hydroxides and potential co-precipitation of the associated elements, e.g. caesium, lead, uranium, etc. [14].

Sulfato-reduction by sulfato-reducing bacteria results in co-precipitation of many elements such as Pb, Cu, Ni, Se, Tc, etc., in the form of insoluble sulfides. This reaction occurs in acid media in strictly anaerobic conditions [15].

Biosorption and bioaccumulation also constitute reactions that can immobilize temporarily the radionuclides. Bio-accumulation relates to most of the elements. Some of them are similar to essential elements, eg. K (Cs), P (Cr), S (As), Ca (Cd) and Zn (Pb) and, in consequence, they will follow the same membrane transport system. Sometimes, accumulation results in the precipitation of metal, as carbonate or phosphate inclusions (Cd, Cu, Pb, Sr, U, Th, Am, Pu, Zn). These properties are currently studied for developing methods of decontamination of waste effluents [16, 17].

2.3 Element-specific microbial processes

Some microbial processes (oxido-reduction and methylation reactions) are element-specific. The anaerobic micro-organisms, in particular the ferri-reducing and sulfato-reducing bacteria, reduce Tc, U, Cr and contribute to decrease their mobility [18, 19]. In addition, the dissimilative reduction of the iron oxo-hydroxides [20] allows the indirect reduction of uranium (VI), chromium (III) and technetium (VII) [21]. Selenium and arsenic can be specifically either reduced or oxidized [4, 22].

Biomethylation is a natural mechanism in which micro-organisms (mainly the sulfato-reducing bacteria) get a methyl group on one or two carbon atoms by the intermediary of methylating agents (e.g. S-adenosyl-methionine and methyl-cobalamine) [23, 24] and eliminate some toxic elements (such as As, I, Sb, Sn...) in forms of volatile compounds.

2.4 Expected global effect

Finally, within the limits of current knowledge, this review results in a schematic classification of the studied radionuclides and trace elements, regarding the role of the micro-organisms on their mobility in surface soils, as follows:

- very important: As, Se, Tc
- moderately important: Cd, Cs, I, Ni, Pb, Pu, Sb, U
- less important: Am, B, Cr, Ra, Sn, Th
- not documented: Be, Nb, Pa

Table 1. Synthesis of the main influence of key microbial mechanisms on the mobility of some trace elements and/or radionuclides.

	Am	As	B	Cd	Cs	Cr	I	Ni	Pb	Pu	Ra	Sb	Se	Sn	Tc	Th	U
Rhizosphere acidification	↗	↘	↗	↗	↗	↗	?	↗	↗	↗	↗	↗	↘	↗	↘	↗	↗
Production of chelating compounds	↗	↗	?	↗	-	↗	↘	↗	↗	↗	↗	-	↘	-	↗	↗	↗
Organic matter degradation	↗	↗	↗	↗	↗	↗	↗	↗	↗	↗	↗	-	↘	↗	↗	-	↗
Biosorption - bioaccumulation	↘	?	?	↘	↘	↘	↘	↘	↘	↘	↘	-	-	↘	↘	↗	↗
Colloidal transport	↗	-	-	?	-	-	-	-	-	↗	-	-	-	-	-	-	?
Co-precipitation of sulfurs/ oxihydroxides	-	↘	-	↘	-	-	-	↘	-	-	-	-	↗	-	↘	-	↘
Reduction of Fe, Mn, S...	-	↘	-	-	-	-	?	↗	-	-	↗	-	?	-	↘	-	↗
Oxidation - dissolution of sulfurs	-	↗	-	-	-	-	-	?	-	-	-	↗	-	-	-	-	-
Bioreduction of the element	-	↘	-	-	-	↘	-	-	-	↘	-	?	↘	-	↘	↘	↘
Bio-oxidation of the element	-	↗	-	-	-	?	-	-	-	?	-	?	↗	-	?	-	↗
Biomethylation	-	↗	-	-	-	-	↗	-	?	-	-	↗	↗	↗	-	-	-

↗ increases the mobility ↘ decreases the mobility ↗↘ may increase or decrease the mobility
 ? potential (not evidenced yet) mechanism - unlikely/not documented mechanism

3. CONCLUSIONS

Currently, no impact assessment model takes into account explicitly the role of the microbial compartment in the soil-plant system. It is supposed that a part of the variability observed on K_d (soil-solution partitioning coefficient) is due to microbial activity. However, it seems essential to explicitly consider the selectivity/specificity of the microbial processes and their controlling parameters. Concerning the extent and the relevance of bibliographical data, many papers describe short term laboratory experiments and large uncertainties remain on the long term effect of microbial activity. In addition, the effect of the soil microbial activity on the behaviour of some elements like antimony and beryllium, or uncommon radionuclides such as protactinium and niobium are somewhat unknown.

However, it is obvious that micro-organisms play a key role in the fate of many trace elements in soil. Their main effects are the modification of chemical reactions and kinetics, i.e., amplification or decrease of an existing process, by transforming the soil physicochemical conditions and the speciation of the element. Micro-organisms may also increase or decrease the accessibility of the solid phase. The impact of microbial activities will be all the more intense that they can catalyse chemically limited reactions and produce a new long-term equilibrium. At last, even if the whole result of the microbial processes is still unknown, they are likely to modify the mechanisms of mobilization or immobilization of trace elements/radionuclides in surface soils.

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