

SPECIATION OF HEAVY METALS AND RADIOISOTOPES

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Summary

The existence of metals and radioisotopes (radionuclides) in a soil environment is transitory since soil is only one component in the wider biogeochemical cycling of elements in an ecosystem. However, the residence time of metals and radionuclides in the soil environment varies considerably and depends on their speciation and the rate of the evolution of soil. The speciation of these elements is fundamental to the chemical and physical reactions they undergo within a soil and consequently determines the mobility and transport between different soil compartments and other environmental systems. The term “speciation” can cover a range of meanings from distribution of a metal between different soil components to the actual chemical form. Despite this ambiguity it is generally recognized that the environmental impact of heavy elements and radionuclides is determined not by the total concentration but by their physical and chemical form within an environmental system. Consequently speciation determines the ultimate fate of heavy metals and radionuclides in terms of transport and uptake in different food chains. An appreciation of the different forms of an element in environmental systems is therefore fundamental in assessing the availability and potential toxic effects of metals in soils to plants and animals.

This article presents a perspective of the important factors, which control the speciation of heavy metals and radionuclides within soils and sediments. It does not attempt to systematically document information on the speciation of individual elements but rather is aimed at considering the sources and examining the chemical and physical processes that occur in soils which are known to control speciation. In addition, consideration is given to current scientific methodologies used to measure and predict speciation and transport behavior with a view to understanding the long-term behavior of metals and radionuclides in soils and other environmental compartments.

1. Introduction

Metallic elements are ubiquitous components of the global environment. Iron, copper, manganese, vanadium and zinc are only a few of the many heavy metals that form an essential part of the natural biogeochemical cycles that sustain life. Heavy metals and some radioisotopes (radionuclides) are widespread natural components of the rocks and minerals of the earth’s crust, and through natural weathering processes and volcanic activity are cycled through the environment (see Table 1). With humankind’s advances in technology and exploitation of ever more of the earth’s resources, the natural cycling of the elements has become increasingly subject to anthropogenic additions of heavy metals and radionuclides, to soil, water and air. The results of widespread industrial and urban pollution are seen on a global scale and the consequences are far reaching. Ecosystems may be unable to incorporate the increased metal burden in their natural cycling of the elements and metals, which may be essential in trace amounts (see *Trace Elements*), become harmful when taken up in plants and animals at increased levels.

Metal	Crustal Abundance ($\mu\text{g g}^{-1}$)
Ag	0.07
Au	0.004

Ba	425
Cd	0.1
Cr	100
Cu	50
Hg	0.05
Ni	80
Pb	14
U	2.8
V	135
Zn	75

Table 1. Average Crustal Abundances of Some Heavy Metals and Radionuclides
Adapted from Alloway B.J. (Ed.) (1994). *Heavy Metals in Soils*, 2nd Edn. Dordrecht: Kluwer Academic Publishers Group.

The term “heavy metal” actually refers to stable metals of density greater than around 5 to 6 g cm⁻³, although they are now often regarded as those discharged as by-products of industrial operations. These include cadmium, copper, lead, mercury, nickel, zinc and the metalloid arsenic and find their way into soils by deposition from the atmosphere, seepage in groundwater from waste sites, direct application of fertilizers and sewage sludge (see *Wastewater Treatment and Reuse for Irrigation, Chemistry of Wastewater*). For the purposes of this article “heavy metals” refers to all high-density metallic elements, which may have hazardous effects on plants or animal ecosystems when present in higher concentrations than found naturally. The concentration and the particular form of a heavy metal, and its interactions with the other components of a soil, determine its potential to cause toxic effects in biological systems. For these reasons the “speciation” or chemical form of a heavy metal is crucial to its behavior in soils and its toxic activity.

Radionuclides differ from “heavy metals” in that they are unstable isotopes of elements (metals and non-metals), which undergo radioactive decay (measured in Becquerels, Bq, where 1 Bq = 1 disintegration per second). Unlike heavy metals it is rarely the chemical form of a radionuclide that determines its toxicity, but the radiation it emits. Radioactive decay involves the emission of radiation, which can be of three types: alpha (α), beta (β) and gamma (γ) emission. During alpha decay a particle consisting of two neutrons and two protons is emitted with a velocity approximately one tenth that of light. In beta decay either a positively charged particle (positron, β^+) or a negatively charged particle (electron, β^-) is ejected. Beta emission energies span a range of energies from essentially zero to a value E_{\max} , characteristic of the radionuclide. In gamma emission high energy electromagnetic radiation is emitted. All three types of radiation present a health hazard, depending on the matter in which the decaying radionuclide is present. For example, alpha particles can penetrate only a few centimeters in air so, although not a great external hazard due to the poor penetrating power, can present a significant toxic affect if inhaled or ingested. Beta particles are rather more penetrating and present both external and internal hazards. The most penetrating are gamma rays, requiring several centimeters of lead to absorb them, and these represent more of an external hazard. All three forms of radiation can alter the

biological workings of plant and animal cells. The toxic effects tend to depend on the energy of the radiation emitted, the extent to which it is retained and the sites within an organism. Radionuclides are often defined in terms of their half-lives, or the time taken for the isotope to decay to one half of its initial activity. Decay occurs exponentially, hence a source containing a radionuclide of half-life 16 days will be half as active after 16 days, one quarter as active after 32 days, one eighth as active after 64 days and so on. Some radionuclides occur naturally in rocks, minerals and plants (e.g. potassium-40, uranium-238, thorium-232), while others are produced artificially in nuclear reactors or weapons (e.g. neptunium-237, plutonium-239, technetium-99). Table 2 summarizes some of the characteristics of the most common radionuclides (*see Radioactivity in Land, Water and Atmosphere*).

Radionuclide	Half-life	Principal radiation emitted	Main occurrence
²²⁷ Ac	21.8 years	β^-	Natural
²⁴¹ Am	4.33×10^2 years	α, γ	Nuclear reactors
¹⁴ C	5.7×10^3 years	β^-	Natural and nuclear reactors
¹³⁴ Cs	2.06 years	β^-, γ	Nuclear reactors
¹³⁷ Cs	30 years	β^-, γ	Nuclear reactors and nuclear weapons
¹³¹ I	8 days	β^-, γ	Nuclear reactors and nuclear weapons
⁴⁰ K	1.3×10^9 years	β^+, γ	Natural
²³⁷ Np	2.14×10^6 years	α, γ	Nuclear reactors
²³⁹ Pu	1.44×10^4 years	α, γ, SF	Nuclear reactors and nuclear weapons
²²⁶ Ra	1.62×10^3 years	α, γ	Natural
²²² Rn	3.82 days	α	Natural
⁸⁹ Sr	52 days	β^-	Nuclear reactors and nuclear weapons
⁹⁰ Sr	28 years	β^-	Nuclear reactors and nuclear weapons
²³² Th	1.41×10^{10} years	α, γ	Natural
²³⁵ U	7.04×10^8 years	α, γ, SF	Natural and nuclear reactors
²³⁸ U	4.47×10^9 years	α, γ	Natural

Table 2. Characteristics of Some Naturally Occurring and Artificial Radionuclides. SF in 3rd column denotes spontaneous fission. Adapted from Wild, A. (1993). *Soils and the Environment: An Introduction*. Cambridge: Cambridge University Press.

The reactions of any heavy metals or radionuclides will depend on their environments. Their chemistry in soil environments is not uniform and the behavior of each heavy metal or radionuclide depends on a complex interplay with the physical and chemical components of the soil. As regards heavy metals, their toxic effects are determined more by the elemental form than the concentration. In the past few decades the importance of chemical form on the behavior of metals, not only in soils but in all environmental matrices, has been clearly illustrated. The Minamata mercury poisoning disaster and “itai-itai” disease, a consequence of cadmium in paddy soils (Japan 1950s), highlighted the influence of the chemical form of a metal on its toxic effects.

It is the importance of this chemical form or “speciation” of metals and radionuclides which is discussed in this article. The objective of continued scientific research into heavy metals and radionuclides in soil systems must be to establish not only the concentrations which are “safe” but also the effects of the different forms of these elements on the ecosystems supported by these soils. Figure 1 indicates the elements in the Periodic Table for which speciation is known to be important in soil environments.

H																	He	
Li	Be											B	C	N	O	F	Ne	
Na	Mg											Al	Si	P	S	Cl	Ar	
K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr	
Rb	Sr	Y	Zr	Nb	Mo	(Tc)	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe	
Cs	Ba	La-Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn	
Fr	Ra	Ac-Lr	(Rf)	(Db)	(Sg)	(Bh)	(Hs)	(Mt)	*									
			Ce	Pr	Nd	(Pm)	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb	Lu		
			Th	Pa	U	(Np)	(Pu)	(Am)	(Cm)	(Bk)	(Cf)	(Es)	(Fm)	(Md)	(No)	(Lr)		

Non metals Light metals Heavy metals

Figure 1. Importance of Speciation for Metals and Radionuclides in Soils

2. Defining Speciation

Initially, scientific interest in the accumulation of heavy metals and radioisotopes (radionuclides) in soils and sediments focused on determination of the total amount of an element present in an environmental sample. Measurements of this gross metal content of soils has a valuable place in characterizing the properties of individual soils and is a measure of their ability to act as a “sink” for metal contaminants. However, for the past few decades there has been recognition that the environmental impact of these heavy elements is determined not by the total concentration but by their physical and chemical form within an environmental system. The ‘physico-chemical’ form or “speciation” governs the behavior of the metal in aqueous, terrestrial and biological systems.

A glance at the available literature, both scientific and general, dealing with metals and radionuclides in environmental systems, shows the diversity of interpretations by different authors of the term “speciation”. Speciation studies vary widely from the operationally defined measurement of distribution of an element in an environmental sample to the full identification of the ions or molecular compounds present (including oxidation states of metals).

The earliest studies of heavy metals and radionuclides in soils and sediments defined speciation in terms of functional designation of a soil phase according to its element content, e.g. the “plant-available” or “mobile” element forms. Operational designation of speciation according to the technique designed to extract the element associated or bound to a particular soil phase is now more commonly used. The use of selective chemical extractants to quantify the element content in a particular soil sample depends on the different solubilities and mobilities of elements in solvents of different strengths and function, e.g. precipitation of an element dissolved in the soil solution or sequential extraction of elements bound to individual soil phases. The speciation of elements extracted in this way is often termed the “acid soluble-fraction”, “exchangeable-fraction”, “oxidizable-fraction” and “residual-fraction”. Operationally defined speciation may also be used to describe the association of the element with particular size fractions in the sample (e.g. < 2 µm particle size soil phases). However, problems have been encountered using such methods of species determination due to the inconsistency of results between different studies. It has been noted that these metal associations with different ‘phases’ are often only nominal and the differentiation between individual phases is unclear.

IUPAC defines a ‘chemical species’ as; “specific form of a chemical element defined as to molecular, complex, electronic or nuclear structure” and ‘speciation’ as “the distribution of a defined chemical species of a element in a system”. This definition tends to restrict the term “speciation” to well identified chemical forms of elements but clearly in analyses of some environmental samples this is often difficult or impossible to achieve with the available techniques. Specific extraction procedures often change the speciation and direct non-destructive methods are generally only sensitive enough to measure major constituents.

At its most fundamental, “speciation” is defined in terms of the oxidation states (valence states) of metal cations in a given environment. The oxidation state determines the coordination (number, type, geometry) of ligands around a metal center and it is these complexes that ultimately affect partitioning of the metals between soil/sediments and solution. Consequently, the solubility of heavy metal and radionuclide complexes in natural systems, under a wide range of environmental conditions, determines their ultimate fate in terms of transport and uptake in different food chains (see *Pathways of Organic Chemical Contamination in Ecosystems*).

An appreciation of the different forms of an element in environmental systems is therefore fundamental in assessing the availability of metals in soils to plants and animals, both as essential nutrients and as potentially toxic elements. For example, natural processes in freshwaters can detoxify the inorganic forms of mercury by

methylation, formation of $\text{Hg}(\text{CH}_3)_2$. However, the resulting methylmercury can concentrate in fish and pose a greater health risk to humans than the original inorganic form. As more and more examples like these come to our attention it becomes increasingly important to define clearly and determine accurately “speciation” of heavy metals and radionuclides in any environmental study. Only then can accurate assessments be made with which to legislate on acceptable levels of these elements in environmental systems and safeguard the quality of life systems.

3. Sources of Heavy Metals and Radioisotopes in Soils

3.1. Historical Trends

One of the major sources of heavy metals in soils is from atmospheric deposition. However, releases of heavy metals into the atmosphere pre-dates the industrial and technological revolutions of relatively recent times. From even the first use of fire by humans, small amounts of heavy metals have been released from burning wood. Later the advent of mining and metalworking techniques markedly increased the anthropogenic input to soils. During the height of the Roman Empire mining of Pb (80 000 to 100 000 metric tons per year), Cu (15 000 tons per year), Zn (10 000 tons per year) and Hg (> 2 tons per year) together with uncontrolled smelting activities resulted in significant releases of heavy metals to the atmosphere. With the industrial revolution came an exponential rise in heavy metal emissions and their dispersal became more widespread due to tall chimneys. The technologies used in mining and smelting have resulted in release not only of the mined metal but also associated byproducts of the mining or smelting process. For example, the mercury amalgamation process used to extract silver from ore deposits in South and Central America, resulted in the loss of 1 gram of Hg per gram of Ag produced. Between 1570 and 1900 there was an estimated release of around 200 000 tons of Hg. The process has continued in more recent times in Brazil to extract gold from Amazon sediments.

Numerous studies have illustrated the long-term trends in heavy metal atmospheric emissions by analyses of preserved natural deposits such as ice cores, aquatic sediments, tree rings, bogs etc. which preserve a record of metal input, in some cases over millennia. Figure 2 is an example of the use of sediment chronology over more recent time periods to estimate the source and deposition history of radioisotopes (radionuclides) released from a point source. Through studies like these valuable information can be obtained about the sources and global dispersion of metals and radionuclides throughout history.

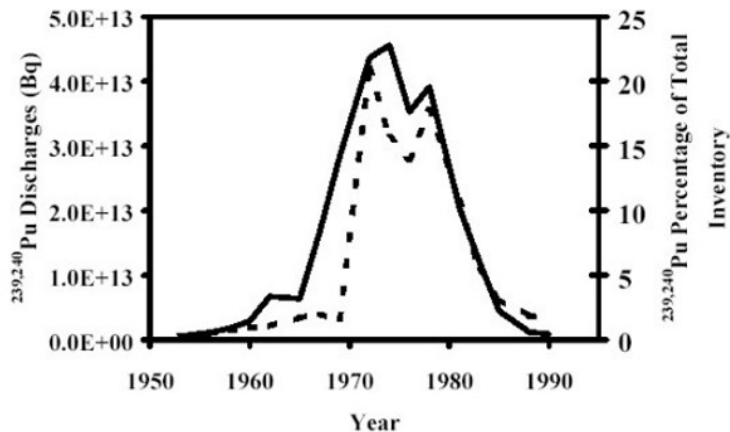


Figure 2. Radionuclide Deposition Chronology in Salt Marsh Sediments

3.2. Present Trends

In recent times, industrial technology and the advent of nuclear fission has resulted in the release of many tons of heavy metals and radionuclides into the atmosphere and to terrestrial and aquatic systems. Approximately 90 percent of outputs from mining activities can be attributed to the 20th century alone. There are many pathways of heavy metals and radionuclides to soils: wet and dry deposition from the air, run-off from land, and intentional and accidental release, all have contributed a substantial anthropogenic load to soil systems (see *Radioactivity in Land, Water and Atmosphere*). Figure 3 summarizes the principal sources of heavy metals and radionuclides to both terrestrial soils and aquatic sediments.

On a global scale the principal sources of heavy metals to soils are from coal combustion (see *Hydrocarbons in the Atmosphere*) and general wastage of commercial products, e.g. corrosion, or usage as chemicals and pesticides. The effects of mining and smelting activities, although performed on a local scale, can affect a much wider area due to atmospheric dispersal of particulates; tipping of solid ore wastes and leaching of acidic metal-containing mine residues has become a significant problem in many mining regions (see *Chemistry of Hazardous and Solid Wastes and Leachates*). Municipal wastes account for the bulk of material put into landfill sites. The large amounts of decomposable organic material increases microbial activity in the site and in some cases can produce volatile methylated metal compounds. On a local scale disposal of sewage sludge on land is one of the most important sources of metal contamination in soils. Although the organic matter can improve soil structure significantly, problems arise when the heavy metal content is too high or application is too frequent or prolonged. Similarly, agricultural processes have for centuries used animal wastes as fertilizers. These, combined with the more recent application of synthetic fertilizers, liming materials and more traditional methods of irrigation and flooding can significantly increase the metal burden of soils if incorrectly implemented. To add to the inventories of naturally occurring radionuclides, the advent of nuclear fission has also seen an increase in the global dispersal of many artificial radionuclides. The nuclear weapons tests of the 1940s-1960s resulted in stratospheric circulation of many artificial

radionuclides around the globe and their subsequent fallout onto soils. Additionally the contributions from nuclear detonations at Hiroshima and Nagasaki, Japan (both in 1945) and a number of specific nuclear incidents (e.g. Chernobyl Reactor explosion in the former USSR in 1986) have increased the widespread dispersal of radionuclides in soils. Local disposals and leaks have lead to contaminated soils at Handford and Savannah River, U.S. and contamination in Lake Karachay in the former USSR. Furthermore controlled release of aqueous radioactive waste to marine environments has been shown to result in accumulation of some radionuclides in inter-tidal sediments and salt marsh soils.

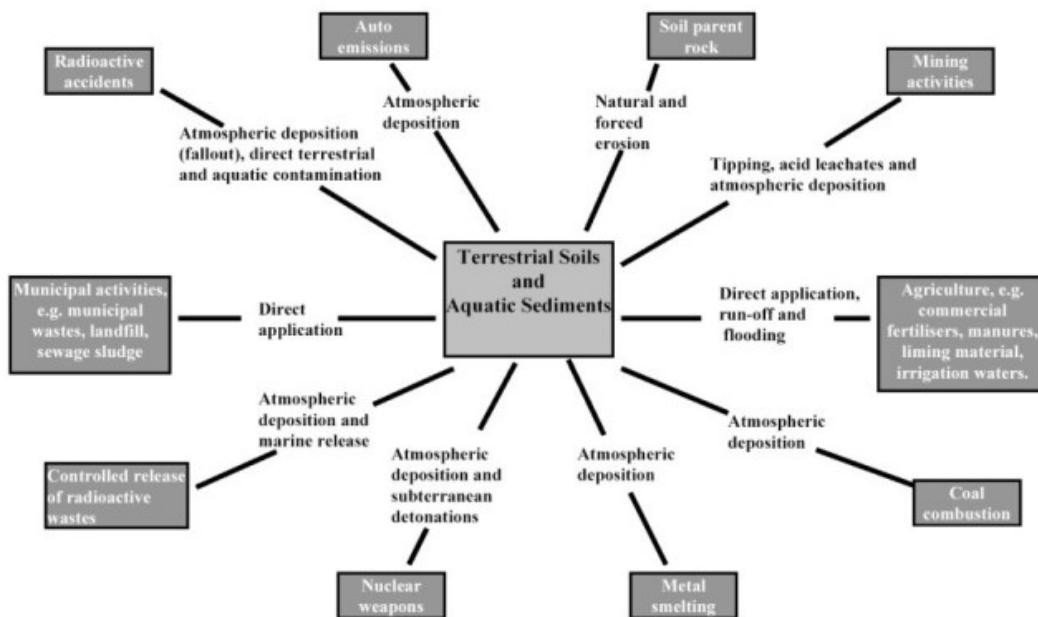


Figure 3. Principal Sources of Heavy Metals and Radionuclides to Soils, Groundwaters and Sediments

Source	Cd	Cr	Cu	Hg	Mn	Ni	Pb	Zn
Agricultural and food wastes	0-3	4.5-90	3-38	0-1.5	15-112	6-45	1.5-27	12-150
Animal wastes, manures	0.2-1.2	10-60	14-80	0-0.2	50-140	3-36	3.2-20	150-320
Atmospheric fallout	2.2-8.4	5.1-38	14-36	0.63-4.3	7.4-46	11-37	202-263	49-135
Coal fly ash and bottom fly ash	1.5-13	149-446	93-335	0.37-4.8	498-1655	56-279	45-242	no data
Fertilizer	0.03-0.25	0.03-0.38	0.05-0.58	no data	0.13-0.83	0.20-0.55	0.42-2.3	0.26-1.1
Logging and wood wastes	0-2.2	2.2-18	3.3-52	0-2.2	18-104	2.2-23	6.6-8.2	13-65
Metal manufacturing solid wastes	0-0.08	0.65-2.4	0.95-7.6	0-0.08	0.41-4.9	0.84-2.5	4.1-11	2.7-19
Miscellaneous organic wastes including excreta	0-0.01	0-0.48	0.04-0.61	no data	0.08-0.63	0.17-3.2	0.02-1.6	0.13-2.1
Municipal sewage sludge	0.02-0.34	1.4-11	4.9-21	0.01-0.8	4.4-11	5.0-22	2.8-9.7	18-57
Peat (agricultural uses and fuel uses)	0-0.11	0.04-0.09	0.15-2.0	0-0.02	5.2-17	0.22-3.5	0.45-2.6	0.15-3.5
Wastage of commercial products	0.78-1.6	305-610	395-790	0.55-0.82	100-500	6.5-32	195-390	310-620
Total input, soils	5.6-38	484-1309	541-1367	1.6-15	706-2633	106-544	479-1113	689-2054

Table 3. Estimated Global Emissions of Heavy Metals into Soils. Figures (in 10^6 kg per year) are derived from global waste discharges and estimated emission factors for 1988. Adapted from Nriagu, J.O. and Pacyna, J.M. (1988). *Quantitative assessment of worldwide contamination of air, water and soils by trace metals*. Nature, vol. 333 (12). Amsterdam: Elsevier.

Table 3 indicates some of the estimated global heavy metal emissions from selected sources into soil systems. Cumulative anthropogenic releases of heavy metals and indeed radionuclides are extensive and in many cases the natural biogeochemical cycling processes of many soils systems have become overburdened and unable to maintain a balance.

4. Soil Processes and Speciation of Heavy Metals and Radioisotopes

The chemical and physical behavior of heavy metals and radioisotopes (radionuclides) in soils depends on the nature of the soil constituents i.e. amount and type of clays, oxides/hydroxides, carbonates, organic matter and colloidal phases and on factors such as pH and redox conditions. More importantly, none of these factors is singular in governing metal behavior in soils, instead a complex interplay of several factors ultimately determines whether the metal (in whatever form) will migrate through the soil solution or be retained within a localized area. This in turn will affect its accumulation and potential toxicological effects in microbial, plant or animal systems.

4.1. Key Factors Affecting Speciation in Soils

4.1.1. Soil pH

Critical to the behavior of metals in soils is the pH of the soil solution. The pH of a soil is dependent on the hydrogen ion (H^+) concentration in the solution present in the soil pores, which is in dynamic equilibrium with the predominantly negatively charged surfaces of the soil particles. The pH is defined in terms of the negative log of the hydrogen ion concentration:

$$pH = -\log[H^+]. \quad (1)$$

Hydrogen ions are strongly attracted to the negative charges on soil surfaces and the 'diffuse' layer of ions close to the surface therefore has a higher concentration of H^+ ions than the bulk solution. In general, natural soils have pH values ranging from 4 to 8.5, due to the buffering action of Al at low pH and $CaCO_3$ at high pH. Generally, at low pH values, free metal cations and protonated anions are mobile, since H^+ ions can displace most other cations at negatively charged soil surfaces. At high pH carbonate and hydroxyl complexes occur, often reducing metal availability.

Table 4 illustrates some of the principal heavy metal and radionuclide species in soil solutions under acidic and alkaline conditions. One example of pH dependent forms of metals in soils is chromium which exists in two stable forms, Cr(VI) and Cr(III). The hexavalent form is more biologically toxic and exists in the soil solution as the chromate anion, $[CrO_4]^{2-}$, in pH-dependent equilibrium with other Cr(VI) forms e.g. $[HCrO_4]^-$ and the dichromate anion, $[Cr_2O_7]^{2-}$. The chromate anion is the predominant form at pH >6. In contrast the less toxic species, Cr(III), is strongly retarded by soil particles at most pH values, being soluble only at low pH. Mobility of Cr(III) decreases

above pH 4 and at $pH > 5.5$ it completely precipitates from solution as hydroxide (see *Acidity and Alkalinity of Soils*).

Metal cation	Acidic soil pHs (3.5-6.0)	Alkaline soil pHs (6-8.5)
Al(III)	Al^{3+} , organic, AlF^{2+} , Al-hydroxy species	$Al(OH)_4^-$, organic
Cd(II)	Cd^{2+} , $CdCl^+$, $CdSO_4^0$	Cd^{2+} , $CdCl^+$, $CdSO_4^0$
Cr(III)	Cr^{3+} , $CrOH^{2+}$	$Cr(OH)_4^-$
Cu(II)	Organic, Cu^{2+}	Cu-hydroxy species, $CuCO_3^0$, organic
Fe(III)	Organic, Fe-hydroxy species	Organic, Fe-hydroxy species
Hg(II)	Organic, $Hg(OH)_2^0$	Organic, $Hg(OH)_2^0$
Mn(II)	Mn^{2+} , $MnSO_4^0$, organic	Mn^{2+} , $MnSO_4^0$, $MnCO_3^0$
Ni(II)	Ni^{2+} , $NiSO_4^0$, organic	Ni^{2+} , $NiHCO_3^+$, $NiCO_3^0$
Np(V)	NpO_2^+	Np-hydroxy and carbonate species
Pb(II)	Pb^{2+} , organic, $PbSO_4^0$	Pb-hydroxy and carbonate species, organic
Tc(VII)	TcO_4^-	TcO_4^-
U(VI)	UO_2^{2+} , organic	U-hydroxy, carbonate and phosphate species
Zn(II)	Zn^{2+} , organic, $ZnSO_4^0$	Zn^{2+} , organic, Zn-hydroxy and carbonate species

Table 4. Probable Heavy Metal and Radioactive Elements' Species in Soil Solutions (Oxic Conditions). Adapted from Ritchie G.S.P. and Sposito G. Speciation in soils. In: Ure A.M. and Davidson C.M. (1994). *Chemical speciation in the environment*. Dordrecht: Kluwer Academic Publishers Group.

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Bibliography

Adriano D.C. (1986). *Trace Elements in the Terrestrial Environment*, New York, Berlin, Heidelberg: Springer-Verlag. [This text provides a comprehensive reference of the biogeochemistry of trace elements and individually details the properties, sources, occurrence and interactions of the major trace elements]

Adriano, D.C. (Ed.) (1992). *The Biogeochemistry of Metals*, Boca Raton; London; New York: Lewis Publishers. [This book is a collection of international contributions on the effects of trace metals on soil quality and their potential threat on transfer through food chains]

Kertsting A.B., Efurud D.W., Finegan D.L., Rokop D.J. Smith D.K. and Thompson J.L. (1999) *Migration of Plutonium in Groundwater at the Nevada Test Site*, *Nature*, vol.397 pp56-59. London: Macmillan Publishers Ltd. [This scientific research paper details the study of radionuclide migration in groundwater colloids at the Nevada test site U.S.]

McNaught A.D. and Wilkinson A. (1997). *Compendium of Chemical Terminology - IUPAC Recommendations 2nd Edn.* Oxford: Blackwell Science Ltd. [A glossary compendium of chemical terminology issued by the International Union of Pure and Applied Chemistry]

Nriagu J.O. (1996) *A history of global metal pollution*, *Science*, vol. 272 pp223-224. Washington D.C.: American Association for the Advancement of Science. [This review article documents some of the major anthropogenic influences, past and present, on global heavy metal pollution].

OECD Nuclear Energy Agency (1999). *Speciation Techniques and Facilities for Radioactive Materials at Synchrotron Light Sources*, Paris: OECD Nuclear Energy Agency. (Workshop Proceedings from the 1st Euroconference and NEA Workshop on Speciation Techniques and Facilities for Radioactive Materials at Synchrotron Light Sources, Grenoble, 1998). [This publication is a collection of contributions from international researchers discussing the uses of synchrotron radiation in the study of radioactive material, with a relevant papers on applications in environmental samples]

Quevauviller P. (1998). *Method Performance Studies for Speciation Analysis*, Cambridge: The Royal Society of Chemistry, U.K. [This book presents all the essential aspects of quality assurance and method performance evaluation in speciation analysis. It details the various analytical methods commonly used in speciation analyses of selected metals and represents the current state-of-the-art in certification and validation of speciation studies]

Salomons W., Forstner U. and Mader P. (Eds.) (1995) *Heavy Metals – Problems and Solutions*. Berlin, Heidelberg: Springer-Verlag. [This book covers aspects of metal pollution in the environment, with reference to specific case studies, and presents some of the current approaches to land remediation].

Sposito G. (1994). *Chemical Equilibria and Kinetics in Soils*, New York, Oxford: Oxford University Press. [A specialist text on the use of chemical thermodynamics and kinetics to describe reactions occurring in the soil solution]

Stumm W. and Morgan J.J. (1995). *Aquatic Chemistry - An Introduction Emphasizing Chemical Equilibria in Natural Waters*, 3rd Edn., New York, Chichester, Brisbane: John Wiley & Sons. [This widely used textbook covers all the essential aspects of aquatic chemistry in natural waters, including chemical equilibria and kinetics, reactions at solid-water interfaces and metal ion aqueous chemistry]

Biographical Sketches

Rose E. Keepax is a Ph.D. student at the Centre for Radiochemistry Research, in the Department of Chemistry at the University of Manchester, UK. She obtained her B.Sc. in Chemistry from the University of Manchester in 2000. During her undergraduate study she also carried out research at various chemical industries and obtained a wide range of analytical experience. The subject of her Ph.D. is the thermodynamics and kinetics of colloidal ternary systems in the environment. It is a highly analytical study focusing on the binding of radionuclides to various types of humic and fulvic acid and the factors influencing their sorption and desorption. She is currently writing up her Ph.D. thesis.

Lesley N. Moyes currently works as a team leader at a large private sector radioanalytical laboratory in the U.K. She attained her undergraduate degree in Environmental Chemistry in 1995 from the University of Edinburgh. After that she moved to the Radiochemistry Section of the Department of Chemistry at the University of Manchester to work on her Ph.D. in Chemistry. During this time her research focused on the geochemical interaction of selected radionuclides with glacial and secondary mineral phases and investigations of surface speciation through X-Ray Absorption Spectroscopy. A subsequent Post-Doctoral Research Associate position at the University of Manchester then focused on the structural

characterization of initially formed mineral phases and in particular on iron, mercury and copper sulfide minerals. After completing her post-doctoral studies she started to work in the private sector, initially as a laboratory manager for a radioanalytical laboratory. Currently, she leads a team focused on radioactive waste management and decommissioning analyses.

Francis R. Livens is Professor of Radiochemistry in the Department of Chemistry at the University of Manchester, U.K. He obtained his first degree, in Chemistry and Geochemistry in 1982, from the University of Leicester. Following this he moved to Glasgow, where he carried out his Ph.D. studies from 1982 and 1985. His Ph.D. was in Environmental Radiochemistry and involved looking at the processes, which control the cycling of radionuclides in the environment, with particular reference to the soil chemistry of plutonium. Following his Ph.D., he moved to Cumbria where he worked for the Natural Environment Research Council's Institute of Terrestrial Ecology, at their Merlewood research station, from 1985 until 1991. Whilst much of this work continued to involve the biogeochemical cycling of radionuclides, the Chernobyl accident of 1986 moved the work more towards fission products and control of their entry into the food chain. Professor Livens joined the University of Manchester in 1991 as a lecturer in Radiochemistry. During his time here he has established the Centre for Radiochemistry Research, which was opened in April 1999. Work undertaken within this research group includes, geochemistry of radioactive elements, coordination chemistry, spectroscopy, electrochemistry and more recently radiopharmaceutical chemistry. Professor Livens' primary research interests remain Radioelement Biogeochemistry and Radioelement Coordination Chemistry.