CHEMICAL SPECIATION, BIOAVALABILITY AND GEOCHEMICAL FORMS OF TOXIC METALS IN POLLUTED SOILS

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The term potentially toxic metals (PTMs) includes essential (e.g., Cu, Mn, Se, Zn, Co) and nonessential (e.g., Hg, Cd, Pb) elements. The elements essential for plants and animals are required in low concentrations and are termed micronutrients, but at high concentrations they may be toxic for plants, animals, and humans. In the soil environment potentially toxic metals (PTMs) are persistent contaminants and it is generally accepted that their distribution, mobility, biological availability and toxicity depend not simply on their total concentrations but, critically, on their forms. These may be soluble, readily exchangeable, complexed with organic matter, or hydrous oxides, substituted in stoichiometric compounds, or occluded in mineral structures. Any changes in in environmental conditions, whether natural or anthropogenic, can alter the forms of PTMs, thereby affecting their behaviour in soil. The main controlling factors include pH, redox potential, sorption–desorption reactions, chemical complexation with inorganic and organic ligands, and time.

Metal bioavailability is the fraction of the total metal occurring in the soil matrix, which can be taken up by an organism and can react with its metabolic system. Metals can be plant-bioavailable, if they come in contact with plants (physical accessibility) and have a form which can be uptaken by plant roots (chemical accessibility). Soil metals become accessible for humans by ingestion, inhalation and dermal contact. Available forms of PTMs are not necessarily associated with one particular chemical species or a specific soil component. Plant roots absorb nutrients from the soil solution, but rarely availability is equated with solubility.

The common determination of PTMs total or "pseudototal" content in soil might minimize the risks for biota and human health, assuming that contaminants transferring to water resources or biota are basically correlated with contamination level. In contrast, relevant paradigms in environmental monitoring, risk assessment and remediation feasibility are the PTMs mobility and availability to microorganisms, plants, animals and humans. For a proper assessment of risk/toxicity (according to PTMs content and availability) of a polluted soil and to predict its attenuation after application of remediation techniques it is crucial to establish the speciation, mobility, and biogeochemistry of the contaminants. In this sense, a requirement exists for analytical methodologies and strategies providing information on the dynamics and behaviour of PTMs in soil.

Speciation science seeks to characterise the diverse forms or, at least, the main metal pools in which PTMs are present in soil. It can be achieved using either direct, mainly non-destructive, or indirect analytical methods. The lecture describes the fundamental principles of soil pollution by PTMs and provides a critical review of the single and sequential chemical extraction procedures that have been widely applied to determine the plant bioavailability and the main geochemical forms of PTMs from contaminated soil. Examples of complementary use of chemical and instrumental techniques and applications of PTMs speciation for risk and remediation assessment will be illustrated.

Key words: soil pollution, bioavailability, speciation, chemical extractions, risk assessment