

Arsenic bioaccessibility: What does soil have to do with it?

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The bioaccessibility/bioavailability of soil arsenic can be estimated by a variety of *in vitro* methods which simulate the human gastrointestinal environment, and through the use of various *in vivo* animal models. These methods produce values which often show poor agreement for a particular soil sample. This study was conducted to identify the soil parameters which influence the bioaccessibility of soil arsenic.

Six soil samples contaminated by different arsenic sources were characterized for grain size distribution, pH, chemical composition, mineral content, arsenic oxidation state, TOC, TIC, and N. The *in vitro* bioaccessible arsenic and *in vivo* relative bioavailable arsenic were previously determined for these soil samples by Basta and Richey (2009) and by Roberts *et al.* (2002, 2007), respectively. Soil arsenic concentrations range from 100-900 ppm, pH values range from 4.7 to 8.0, and TOC ranges from 0.8-9.6 % by weight. The soils also vary significantly in their major, minor and trace element compositions, as determined by microwave-assisted acid digestion. Arsenic is present in all soil samples as As (V).

Statistical analyses are being used to identify soil parameters which are correlated with, and therefore likely control, arsenic bioaccessibility. In general, bioaccessible arsenic is inversely correlated with soil grain size and positively correlated with soil TOC, aluminium, iron and calcium concentrations, although these relationships are complex and inconsistent. Principal component analysis is being used to help elucidate the complex relationships between soil characteristics and soil arsenic bioaccessibility.

The role of speciation in geo- and environmental analysis: Crossing boundaries

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Biogeochemistry aims at studying the fate and transfer of major and trace elements between different compartments of the biosphere and the geosphere. Major and trace elements occurs in a variety of forms such as free ions, inorganic complex, organometallic complex, biomolecules up to higher less structured fluvic-humic complex. All these different entities containing metals in their chemical structures have totally different physico-chemical properties resulting in different reactivity, stability and finally control their transfer and fate between the different compartments of the environment. Speciation is the underlying key to promote the transfer of metal species through different boundaries such sediment to water, particles to water, and water to air. The chemical properties of metal species are also key factors to promote both toxicity of bioaccumulation in the biota.

These concepts are being greatly facilitated by the introduction of ICP/MS as detector in environmental sciences. Indeed, the development of ICP coupled to a variety of mass analyzers such as first a quadrupole, then a detector with a sector field analyzer and more recently with a multi-collector detector has allowed promoting a full reassessment of environmental evaluation. Resulting improvements in environmental sciences have been essential in refining and reassessing metal species transfer between environmental compartments due to the sensitivity and selectivity of the systems.

Finally the recent introduction of Multicollector ICP/MS has even further extended the ways to promote environmental assessment. The high precisions obtained on a routine basis coupled to transient signal possibilities have allowed promoting the direct understanding of reactivity using isotopic fractionation signatures. These developments have even brought a new dimension in environmental assessments with the recent promotion of Mass Independent Fractionation (MIF) now directly evidenced for heavy elements such as Hg with modern MC ICP/MS.

We will illustrate these different points and highlight the great benefit that ICP/MS as brought to the "reassessment" of environmental reactivity and pathways of metals species opening up new concepts and understanding of the fate of elements in the biogeosphere.