VALIDATION OF THE METHODS FOR HEAVY METAL SPECIATION IN SOILS AND SEDIMENTS

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The knowledge of the chemical forms of metals is used to assess their availability and uptake by plants, and in sediments the forms of metals determine their transport and mobility in the aquatic media. This information may be obtained by determining chemical forms of metals (speciation) or different phases in which the metals are bound, obtained by applying extraction schemes. The analytical methods used include different steps and all of them must be validated. We report here the recommendations to minimize the errors in this kind of analysis. For validation the use of Certified Reference Materials (CRMs) and the participation in interlaboratory exercises are highly recommended.

Speciation of metals in soils and sediments

Environmental studies on heavy metals in soils and sediments can be considered from two different aspects: knowledge of the total content, to provide useful information to establish the hot spots or for mapping a polluted zone, and on the other hand knowledge of the chemical forms of the metals. This knowledge determines the availability of metals in soils and their uptake by plants and it is also useful in biogeochemical studies. The chemical forms of metals determine the behaviour of the sediments since although these materials are considered as the final sinks of heavy metals they can also act as a source of contamination when significant changes of pH, redox potential, salinity, particulate matter or microbial activity occur in the environment. These changes can increase the mobility and transport of the metals in the aquatic media (1-3).

The toxicity of an element is closely related to its chemical form, and so the quantification of these chemical forms is necessary to assess this toxic effect (4,5). Thus not only the total concentration but also the concentration of the different forms of metals must be determined in these materials.
Methodology. Sources of error and validation

To determine the metal species in soils and in sediments two approaches have been proposed. One of them consists of the determination of well-defined chemical species, such as different oxidation states of an element, for instance As(III) and As(V), or organometallic compounds, such as methylmercury or dimethylmercury. This kind of analysis is properly known as speciation. Another approach is less specific and allows the determination of the physical and chemical forms of an element bound to the different phases of the soil or the sediment, e.g. carbonate, iron and manganese oxides, organic matter, sulfides or bound to structural silicates, by applying well defined extraction schemes, like for instance sequential extraction procedures (6,7).

These approaches are supported by appropriate analytical processes, including different steps, each of which contributes to the uncertainty of the final result. However irrespective of the method used it is essential to preserve the integrity of the metal species, since sampling, storage, pretreatment, extraction or final measurement can alter the original species. The danger of significant changes in metal species must be considered, especially when the species are unstable or the soils or sediments are sensitive to pH or redox potential.

It is widely recognized nowadays that the use of validated methods is the only way to assess the quality performance of analytical laboratories (8). The validation is more difficult for metal speciation methods than for the methods for total metal analysis. The difficulty arises from the complexity of the samples and from the instability and vulnerability of many of the metal species during the analytical process, and efforts have to be devoted to achieving good and reliable results that can be further used to take remedial actions and to support political decisions.

Taking into account the steps to be considered for metal speciation in soils and sediments (Fig. 1) some comments and recommendations are now reported, to be taken in consideration to minimize the errors associated with each step.