

# Partitioning of trace elements in different world river sediments by chemical extraction technique

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The mobility, the transport, and the toxicity of trace elements in aquatic systems depend on the chemical form of the elements which is controlled by the physico-chemical and biological characteristics of that environment such as salinity, pH, redox potential, and concentration of chelators. In order to study the bioavailable fraction of river sediments, an analytical procedure involving sequential chemical extractions (soluble with water (eau), really exchangeable (ech), bound to carbonates (carb), manganese oxides (MnO), amorphous iron oxides (AFeO), crystalline iron oxides (CFeO) and organic matter (org)). This procedure has been developed from an improvement of Tessier *et al.* (1979) and Schuman (1985) procedures to determine the speciation of: Si, Ca, Fe, K, Mn, Al, Co, Rb, Sr, Y, Sb, Cs, Pb, U, Th and the lanthanides on several river sediments from Argentina, Brazil, France and Morocco.

## Experimental

The leaching procedure (see Table 1) takes place in a watertight container to prevent evaporation, with continuous agitation to increase the interaction surface between the reagent and the sediment. The indicated quantities refer to 1 g sediment (dry weight at 100°C) of the original sample used for the initial

extraction. After each reaction, the residue is filtered with 0.45 µm pore size Millipore filters (ref HAWP) made of polyvinylidene of fluorure (CHR-CFF-n) and washed with 20 ml of distilled water. Then the leachate is stored in a polypropylene bottle at 4°C until chemical analysis, whereas the residue (dried at 40°C in order to prevent any dilution of the following reagent) undergoes the following extraction step. The percentage of each element in the various fractions was calculated on the basis of the total element concentration which was determined by digesting the sample by either a tri-acid attack or an alkalinemelting attack.

The efficiency and the selectivity have been evaluated for each step thanks to :

(1) six TOT clay minerals: three smectites (montmorillonite, Clarsol and Colclay), one muscovite, one stevensite and one saponite.

(2) three carbonates: a synthetic calcite (Prolabo), natural calcite and dolomite.

(3) five synthetic and natural manganese and iron oxides: (a synthetic manganese oxide from Koch Light Laboratories, two synthetic iron oxides from Schering A.G. Berlin and from Merck and two natural iron oxides (from Atlantis II, carott 1032 VIII 1-6 and carott 1032 XI 75-80).

The technique was found to be satisfactory, with no pollution problems, a good efficiency and a good

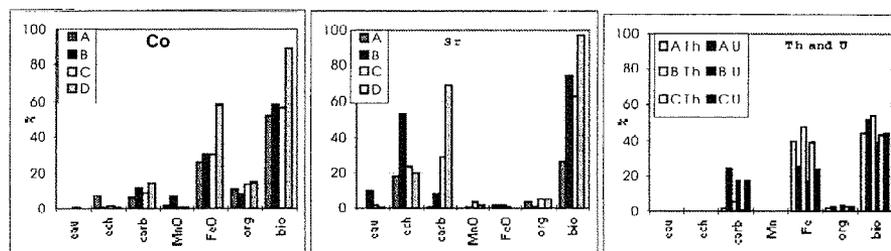


FIG. 1. Percentage of leached Co (left side), Sr (centre) and Th and U (right side) on Rio Coyle (Argentina), 12/96 (A), Piracicaba (Brazil), n°8, 01/97 (B), Ill (France), 05/96 (C) and Sebou (Morocco), mbk,05/97 (D) sediments.

TABLE 1. Protocol summary of the new 7-step sequential extraction procedure

Fraction	Reagent	Time	pH
eau	10 ml water	30 min	5.7
ech	10 ml of 1 M $Mg(NO_3)_2$	2 h	5.0
carb	10 ml 1 M NaOAc, pH = 4.50	5 h	4.5
MnO	10 ml 0.1 M $NH_2OH HCl$	30 min	3.5
AFeO	10 ml { 0.2 M $(NH_4)_2C_2O_4$ - 0.2 M $H_2C_2O_4$ } in the dark	4 h	3.0
CFeO	10 ml { 0.2 M $(NH_4)_2C_2O_4$ - 0.2 M $H_2C_2O_4$ - 0.1M $C_6H_8O_6$ , T = 80°C	30 min	2.3
org	1) 3ml 0.02 M $HNO_3$ and 8 ml of 35% $H_2O_2$ , T = 85°C. 2) 5 ml 3.2 M $NH_4OAc$	5 h 30 min	2.0

selectivity for each step. The repeatability has been tested thanks to four identical samples (bottom sediments from the Garonne river) which have been leached by this sequential extraction procedure. The standard deviations of the total leachate element for the four replicate analyses is below than 3% for all the tested elements.

## Results and discussion

Thanks to this new sequential extraction procedure, the characteristics of 37 solid phases being exported via different rivers (Rio Chico, Rio Colorado, Rio Coyle and Rio Deseado (Argentinian rivers), Piracicaba and its tributaries (Brazilian rivers), Garonne and Ill (French rivers) and Sebou and its tributaries (Moroccan rivers)) have been studied.

Predictably, the intensity of the leachate varies according to the different samples; in general the Argentinian samples, which are poor in carbonate and organic fractions, are less leachable than the other samples. Nevertheless, whatever the origin of the sample, the elements which belong to a same chemical family have a similar leachate profile. For example, the alkalines (Rb, Cs), silicium and aluminium stay linked to the residual fraction.

On the contrary, metals (Fe, Mn, Co and Pb) are very bioavailable; 30–60% and 50–100% of the cobalt are available respectively in Argentinian and

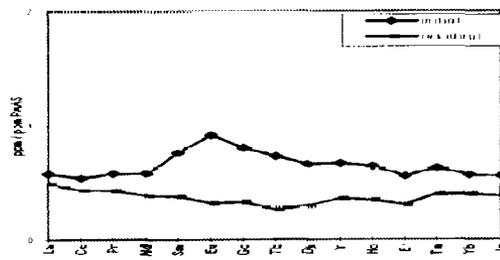


FIG. 2. PAAS normalized REE distribution on a Moroccan sediment (MJ 01/05/97).

Brazilian, French and Moroccan sediments (Fig. 1, left). Up to 78% of lead is bioavailable in French river suspended matters. Metals are mainly controlled by iron and manganese oxide fraction, but they are sometimes present in the carbonate or organic fractions too. Similarly, Sb is exclusively associated with iron oxides.

Both Sr and Ca are very bioavailable (between 40–90%, 40–65% and 65–100% of the total Sr is bioavailable in Brazilian, French and Moroccan river sediments, respectively) and they are mainly associated with the exchangeable and carbonate fractions (Fig. 1, centre). Only these two elements are significantly bound to exchangeable sites.

The actinides (U and Th) present often two kinds of profiles: Th is mainly associated with the oxides whereas U is linked at the same time to the oxides and to the carbonates (Fig. 1, right). Nevertheless, for a given sample, uranium and thorium have the same bioavailability, which is very different from a sediment to another (between 7–82%).

The rare earth elements (REE) are mainly linked to the carbonates, organics and iron oxides. We can notice that the PAAS normalized distribution of the total sample could be different from that of the residual fraction (Fig. 2). So we can predict a fractionation of REE during the fluvial transport.

## References

- Tessier, A., Campbell, P.G.C. and Bisson, M. (1979) *Anal. Chem.*, **51**, 844–51.
- Schuman, L.M. (1985) *Soil Sci.*, **140**, 11–22.