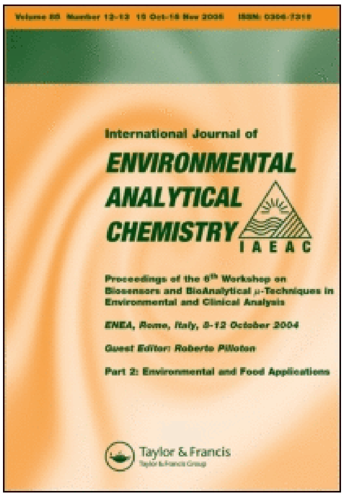

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Speciation of Heavy Metals in Polluted Soils by Sequential Extraction and ICP Spectrometry

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Heavy metals were leached from various polluted soils by selective extraction reagents (water, $BaCl_2$, acetate buffer + EDTA, HNO_3) in order to establish the distribution of the chemical species of Cd, Zn, Cu and Pb. The leachates were directly injected into a plasma spectrometer in order to analyse immediately the extraction solution. This continuous on-line analysis gives qualitative information about the chemical behaviour of each element in function of the type of soil. It permits also to modify the extraction procedure for each sample studied by adjusting the volume of the extraction solution, the time of extraction, or by choosing another extraction reagent more adapted to the sample.

The sum of the respective fraction is in rather good agreement with the total analysis of the soil.

KEY WORDS: Heavy metals, speciation, inductively coupled plasma spectrometry, polluted soils.

INTRODUCTION

Assessing the environmental impact of heavy metals in plants, soils or sediments needs generally more information than a total elemental analysis of the polluted samples. In particular, it may be very helpful to obtain information on the "degree of availability" of toxic materials and as much as possible, absolute specification of the chemical form which is responsible for undesirable effects. Practically, this may be done by selective extractions of specific fractions of heavy metals with appropriate reagents.[1-2] Nevertheless, the large number and diversity of methods which have been proposed for that purpose, indicates by itself their speculative character.[3-6] Each environmental system may indeed require individual investigation and the relevance of the approach proposed for a given system should always be critically assessed for any new system.

In the present paper, we suggest an improvement of the sequential extraction procedures by connecting the outlet of an extraction column to an inductively coupled plasma spectrometer which analyzes directly and continuously the extracted metals. The "on-line" analysis permits indeed to modify the extraction procedure during the extraction itself. At the same time, it gives information on the physico-chemical behaviour of pollutants in presence of various releasing agents.

EXPERIMENTAL

All of the trace elements are found in soils or sediments in chemical "pools" which are listed below:

1) H_2O-soluble ions
2) easily exchangeable ions
3) strongly adsorbed, chelated or complexed ions
4) secondary clay minerals and metal oxides
5) primary minerals or highly fixed ions.

The first pool is simply estimated by extraction with water. Concerning the other forms of heavy metals, various schemes are available in the literature for their speciation. They have been reviewed recently by Pickering[1] and Florence.[2]

The exchangeable ions are commonly extracted by the reagents used for the CEC determination (KCl, $MgCl_2$, $BaCl_2$, ammonium acetate...). The chelated ions are extracted by a strong chelating agent as EDTA, DTPA, ammonium lactate, etc... By virtue of their chelating power, they remove most or all of the adsorbed and complexed forms of metals. If they are used with an acetate buffer ($pH = 4.8$), they dissolve also many other compounds where the metal could not be called "exchangeable", but where it is potentially available (ex.: carbonates, phosphates, some sulfates,...). The fourth fraction is determined by extraction with diluted strong acids (HNO_3 or HCl 0.1 or 1 N), and the last fraction is estimated by the metals remaining after the other extractions or by the difference between the total analysis and the sum of extracted metals.

In our experiments, a small column of 0.5 cm diameter was packed with 1 g of polluted soil and eluted successively with distilled water, $BaCl_2$ 0.1 M, acetate buffer (0.1 M)+EDTA (0.05 M) and HNO_3 (10% w/v) furnished by a peristaltic pump as shown in Figure 1. The death volume of the column was filled with acid washed sand. The extraction solution was fed to the ICP spectrometer through the capillary tube, together with a continuous flow of distilled water.

Extraction solution delivery rate to the soil column via the peristaltic pump was 0.75 ml/min., while a 0.5 ml/min. rate was used for the ICP pump. These flows have been chosen to obtain a compromise between a maximum sensitivity and a reasonable timing for a complete extraction.

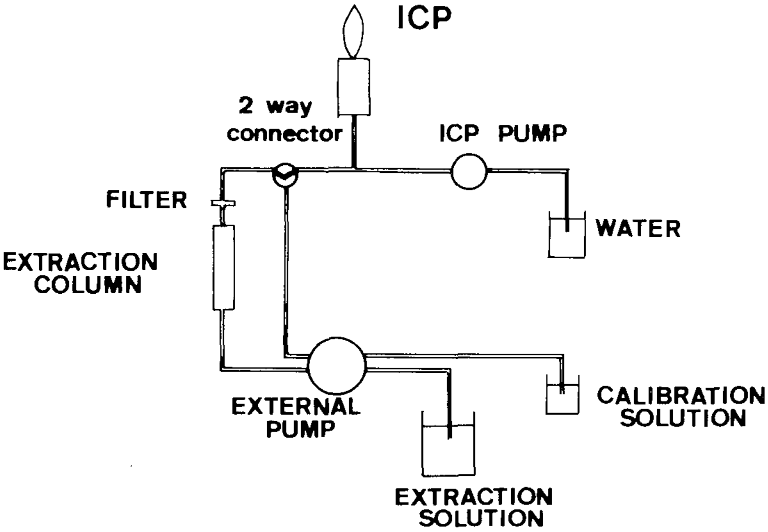

Figure 1 Schematic representation of the elution system.

An Instrumentation Laboratory Inc. IL Plasma-200 ICP emission spectrometer was used. The instrument was in dual channel form using Rev. 6 software. The sequential mode of reading of this spectrometer limits the number of elements which may be analyzed in that type of experiment. Indeed, if the number of analyzed elements increases, the delay between two readings increases and the shape of the extraction peaks is not correctly registered. Notwithstanding the fact that is not an ideal situation, it has been possible to study four elements: Cu, Zn, Cd and Pb.

Zn and Cd were measured respectively at 213.86 and 214.44 nm in channel B; Pb and Cu at 220.35 and 224.7 nm in channel A.

The 224.7 nm line of Cu was chosen for its proximity of the 220.35 nm line of Pb, what permits to improve the rate of the analysis. The reading time was 0.5 s for each element and the line intensities were transmitted for treatment to an external micro-computer (Tandy model 2) equipped with a high resolution graphics screen. The delay between two measurements was less than 1 minute. The emission intensities were plotted on the computer screen in function of the time and stored on disk for later treatment. A two-way connector after the soil column permits to calibrate the spectrometer by introducing known volumes of standard solution before or after the extraction.

The samples studied were acidic sandy soils (BN samples) and neutral loamy soils (E samples). They have been collected near zinc smelters at various depths of the soil profile and they are described elsewhere.[7] A river sediment formed in anoxic conditions has also been added (R 107).

RESULTS AND DISCUSSION

Figure 2 shows the raw data for a typical acidic sandy soil (BN 7) as obtained on the computer screen without any transformations. The line intensities are plotted as a function of time for the 4 elements studied.

The BN 7 soil is of the podzolic type consisting essentially of sand and humus. It has been sampled from the humus accumulation zone at a depth of 30 cm. We have shown previously that the availability of Cd and Zn is very high while Cu and Pb are more strongly fixed

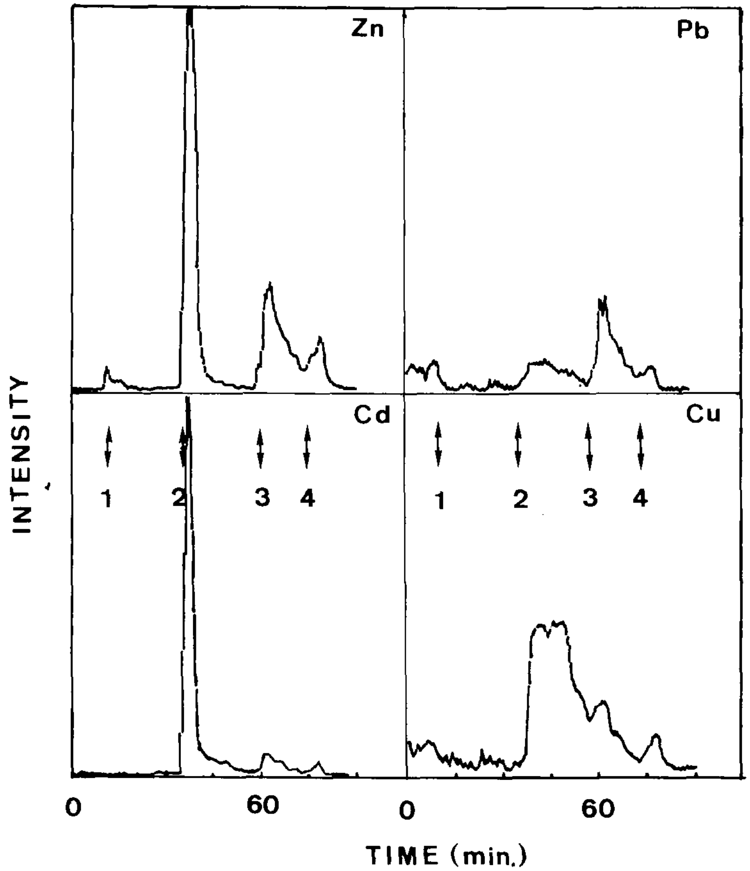

Figure 2 Line intensities of Zn, Cd, Pb and Cu during successive leaching of an acidic sandy soil (BN 7) by 1: H_2O, 2: $BaCl_2$, 3: acetate buffer+EDTA, 4: HNO_3 (10%).

by organic matter.[7,8] This appears clearly from Figure 2. Cd and Zn are essentially extracted by water and $BaCl_2$ while Cu and Pb are extracted by EDTA and diluted acid. Furthermore, the peaks of Cu and Pb are less resolved, due to a contribution of the residual fraction.

In the upper layers, Cd and Zn are more recently deposited and they are less available. This is shown in Figure 3 for three soil

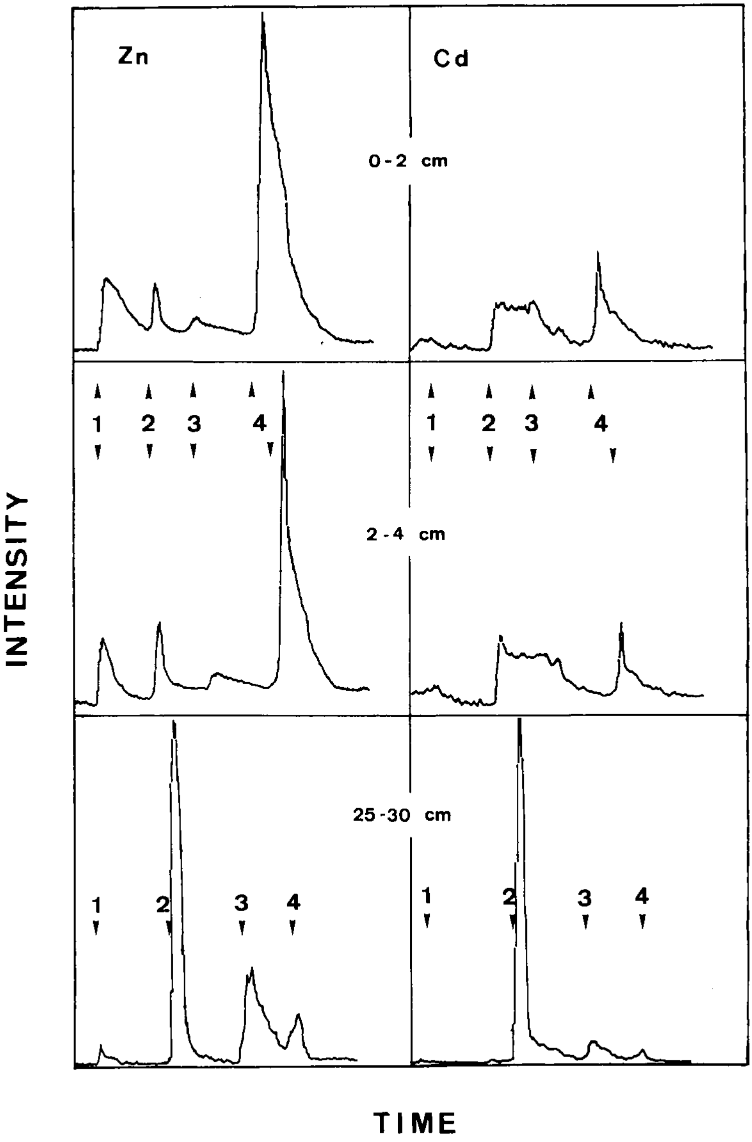

Figure 3 Zn and Cd emission for a polluted acidic sandy soil sampled at various depths, Leaching by 1: H_2O, 2: $BaCl_2$, 3: acetate buffer + EDTA, 4: HNO_3 (10%).

samples taken at various depths (0–2, 4–6 and 25–30 cm). The peaks due to the less available fractions (3 and 4) are more important in the upper layers and there is an increase of the first peaks in the deeper layers. Qualitative informations on the physical behaviour of heavy metals are thus obtained from these type of experiments.

The application of this method has also been tested for a polluted loamy soil and a river sediment.

As these samples contain clays, clogging of the filter is observed. Nevertheless, by mixing the sample with acid washed sand, it has been possible to realize the complete scheme of extraction. The results are shown in Figures 4 and 5. In this case also, qualitative

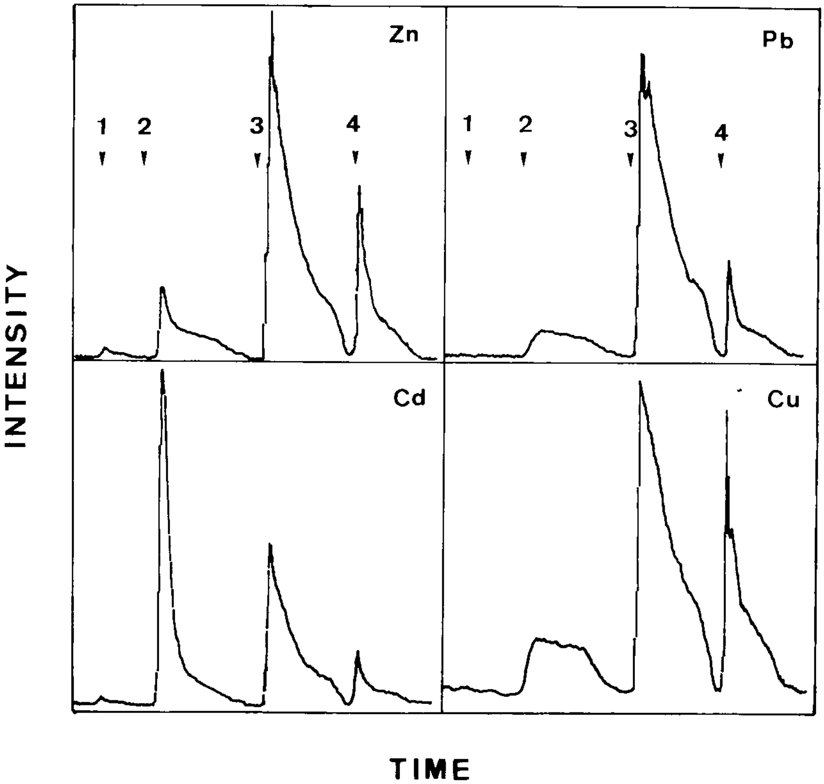

Figure 4 Line intensities of heavy metals during successive leaching of a neutral loamy soil (E 4). 1: H_2O, 2: $BaCl_2$, 3: acetate buffer + EDTA, 4: HNO_3 (10%).

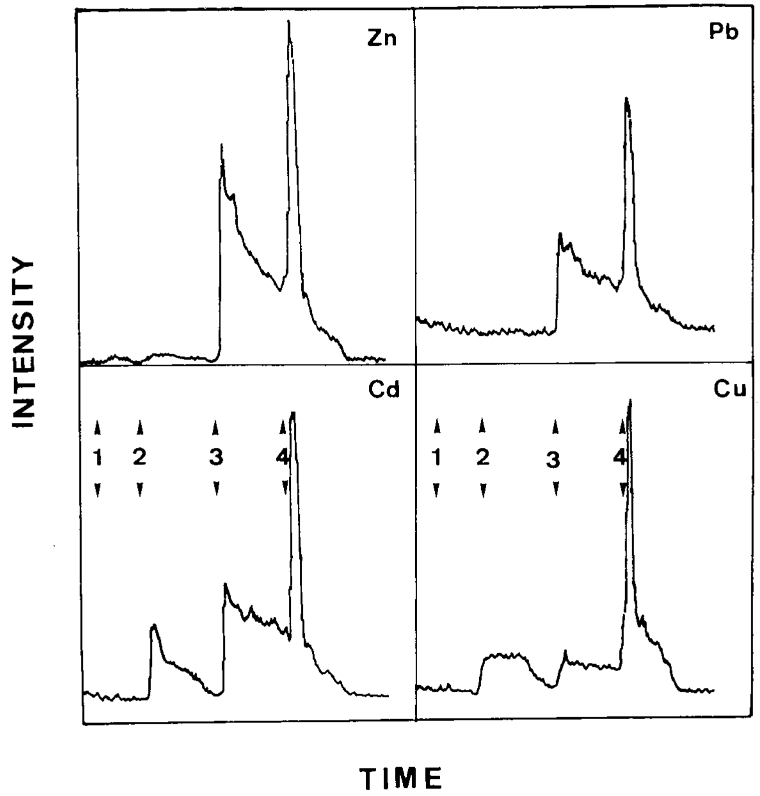

Figure 5 Line intensities of heavy metals during successive leaching of a river sediment (R 107). 1: H_2O, 2: $BaCl_2$, 3: acetate buffer+EDTA, 4: HNO_3 (10%).

informations on the chemical species are obtained. Indeed, in neutral loamy soils, the heavy metals are mainly immobilized as carbonates and phosphates or highly adsorbed on clays and free oxides.[7–8] They are thus extracted mainly by the acetate buffer+EDTA as it appears in Figure 4 for Zn, Cu and Pb. An important fraction of Cd is also extracted by $BaCl_2$, reflecting the higher availability of this metal.

In the river sediment, the heavy metals are deposited in anoxic conditions, mainly as sulfides, so that they cannot be extracted by medium strength extraction agents. Consequently, the first extraction peaks are small and not resolved and the last peak is the most important for each element studied (Figure 5).

Attempts have been made to quantify the extracted metals. For that purpose, various known volumes of 5, 10 and 15 ppm solutions of each metal have been injected by the outer peristaltic pump via the two-way connector. Integration of the emitted signal has been done by multiplying the line intensity by the time between two measurements which is given by the spectrometer. Calibration curves obtained are perfectly linear as illustrated in Figure 6. They give calibration coefficients which permit to integrate the data of the extraction peaks stored in the external computer. The heavy metals extracted by each reagent are reported in Table I. The residual fraction remaining after the complete scheme of extraction has been

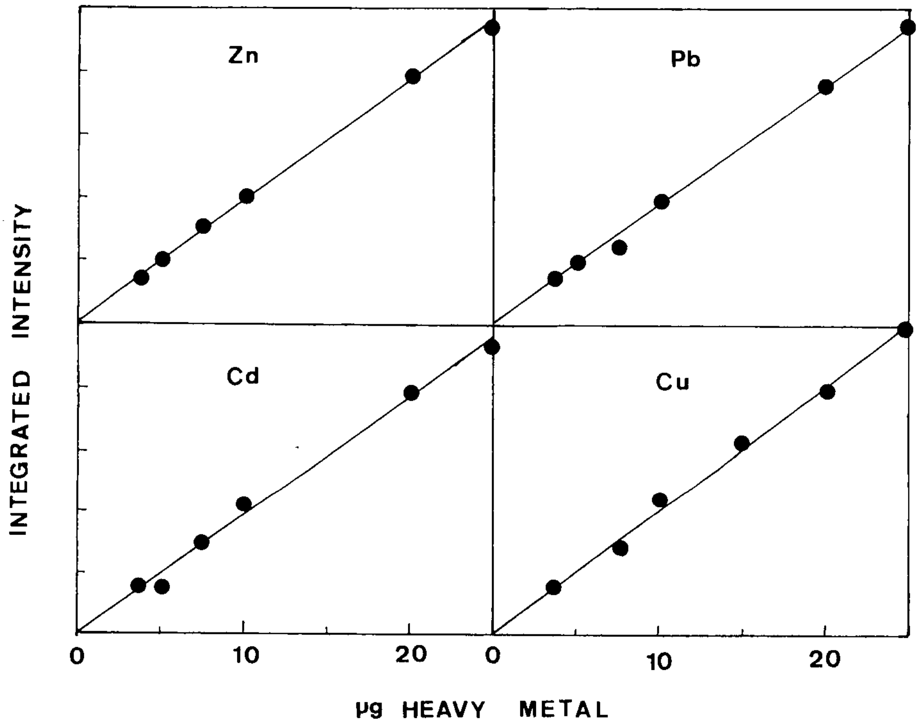

Figure 6 Calibration curves for the elution system.

Table I Comparison of the total analysis and the sum of each fraction extracted by selective reagents

Sample	Cd (mg/kg)		Zn (mg/kg)		Pb (mg/kg)		Cu (mg/kg)	
	Total analysis	Sum of species	Total analysis	Sum of species	Total analysis	Sum of species	Total analysis	Sum of species
BN 2	3.7	4.8	336	490	1483	1327	163	172
BN 7	31	29	365	450	28	27	15	20

measured independently after a HNO_3-HCl mineralization procedure. The sum of metals extracted by each reagent is in agreement with the total analysis of the sample with a disparity below 20% what may be considered satisfactory taking into account the lack of precision of the complete method.

CONCLUSION

The direct control of the extraction solution of soils by "continuous flow injection" in a plasma spectrometer permits to obtain very interesting information on the chemical behaviour of trace elements in presence of various releasing agents. It gives indeed a kind of "chromatogram" of the chemical species of the elements studied which may be considered as a picture of their availability. It permits also to adapt the soil/solution ratio for each sample by increasing the time of extraction.

By using a simultaneous plasma spectrometer, it should be possible to extend this type of analyses to a greater number of elements. It should also be possible to apply this technique to the speciation of major elements of great interest for the agronomists (phosphorus in particular).

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