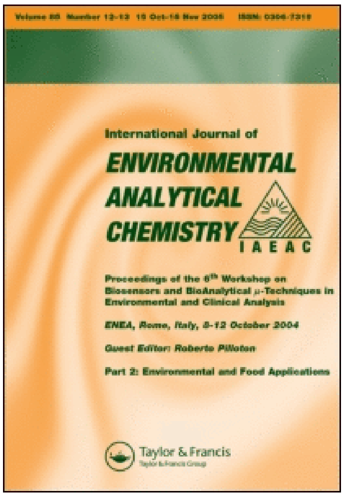

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Speciation of Metals in Soils[†]

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Our studies have centred around the speciation of cadmium and manganese in three soils, one of which has been amended with sewage sludge. We report here some of our preliminary results, obtained by a coupled high performance liquid chromatography (HPLC)—graphite furnace atomic absorption spectroscopy (GFAAS) technique.

The results indicate that cadmium may exist in different forms in soil, but only one form in soil-pore waters. Manganese is present in different soil-pore waters in different forms. The presence of sewage sludge in the soil can also affect the quantity and form of metals in water extracts.

KEY WORDS: Speciation, soils, cadmium, manganese, HPLC.

INTRODUCTION

In recent years, interest in determining the speciation of trace elements in environmental samples has increased. This interest has arisen largely because of the awareness that it is the chemical species, rather than the element itself, that plays the important role in the transfer of elements along the water-soil-plant-animal-human chain.

Measurement of the total concentration of a trace element provides inadequate information to allow us to assess the bioavailability or toxicity of that element. For example, we know that the human body only readily absorbs cobalt in the form of

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cobalamin (Vitamin B12).[1] We also know that chromium VI is toxic to most organisms while chromium III is an essential trace element.[2]

The requirement and the techniques available for studies of speciation of trace metals in waters, have recently been extensively reviewed.[3] The need for speciation studies of radionuclides released into the environment has also recently been underlined.[4]

The studies we report here concern the speciation of some metals in soils. The soils studied have been used at Harwell for several years to study the migration of radionuclides between soil and plants, mainly grass and clover, but including some vegetable crops. These earlier studies concentrated on measuring the transfer factors of radionuclides between the soil and vegetation grown under laboratory and field conditions.[5]

This paper presents some of our preliminary results for cadmium and manganese extracted in pore-waters of two soils and a sewage sludge amended soil, using a combined liquid chromatography-optical spectroscopy technique. Cadmium and manganese were chosen as elements representing the heavy metals and transition metals respectively. Additionally cadmium is an element of general environmental interest, while manganese is an element of interest in the nuclear fuel cycle. Also, both elements appear to play an important role in human biochemistry.

EXPERIMENTAL

Three soils have been studied. These are designated WS (a sandy soil collected from a coastal industrial site), TF (a clay soil from an inland industrial site) and SS (WS soil amended with sewage sludge). These soils were chosen as they were expected to be free from contamination by ores or mining wastes. The WS and TF soils have been stored untreated since collection, while the SS soil has been used in a greenhouse grass-growing experiment.

The soils were oven dried at 60°C for two hours and then sieved through a 1 mm nylon mesh to remove stones and fibrous matter. Manganese and cadmium levels were determined by an aqua-regia extraction of the soils, followed by dilution and analysis by Inductively Coupled Plasma—Optical Emmission Spectrometry using a Bausch and Lomb ARL 3560 instrument.

Soil pore-water solutions were prepared by placing 20 g of sifted soil in a modified polythene centrifuge tube with 10 ml of distilled water. These were allowed to stand overnight, then centrifuged at 2500 rpm for 15 minutes to extract the water.

Samples were chromatographed on a Hamilton PRP-1 column, using a Waters Associates HPLC system. The eluent used was 0.05 M KCl. The buffer was used to maintain a constant ionic strength, and to overcome problems associated with metal ions absorbing onto the column. Flow rates were typically 1 ml/min.

The eluent was monitored with a variable wavelength UV detector set at 255 nm, to detect organic material being eluted. 0.5 ml fractions of the eluent were collected with a Pharmacia (UK) Ltd FRAC-100 automatic fraction collector and were transferred to a Perkin Elmer 503 atomic absorption spectrometer fitted with an AS40 autosampler and HGA-74 graphite furnace unit. 20 μl aliquots of each fraction were sampled and analysed in duplicate. Deuterium arc background correction was used throughout, to compensate for non-atomic absorption arising from the high salt content of the eluent.

RESULTS AND DISCUSSION

Some basic data on the soils and sewage sludge studied are listed in Table I. HPLC-GFAAS traces for cadmium and manganese for the three soil samples (WS, TF and SS) are shown in Figure 1. The continuous trace is the U.V. detector response at 255 nm, while the bar graph represents the GFAAS response to the fractions collected, after 250 μl of soil-pore water had been injected into the HPLC.

The soil-pore water from TF soil contained no detectable cadmium. This was presumably due to the relatively high cation exchange capacity of the soil (compared with the WS soil) as the pH, organic content and cadmium levels of the soils themselves were very similar. The cadmium traces for the WS and SS soils were qualitatively very similar. Only one cadmium form was seen, co-eluting with the organic matter. The cadmium appeared at the same retention time as a standard solution of Cd^{2+} (as chloride), and could not be further resolved with additional different HPLC columns in series. These results were consistent with those of other

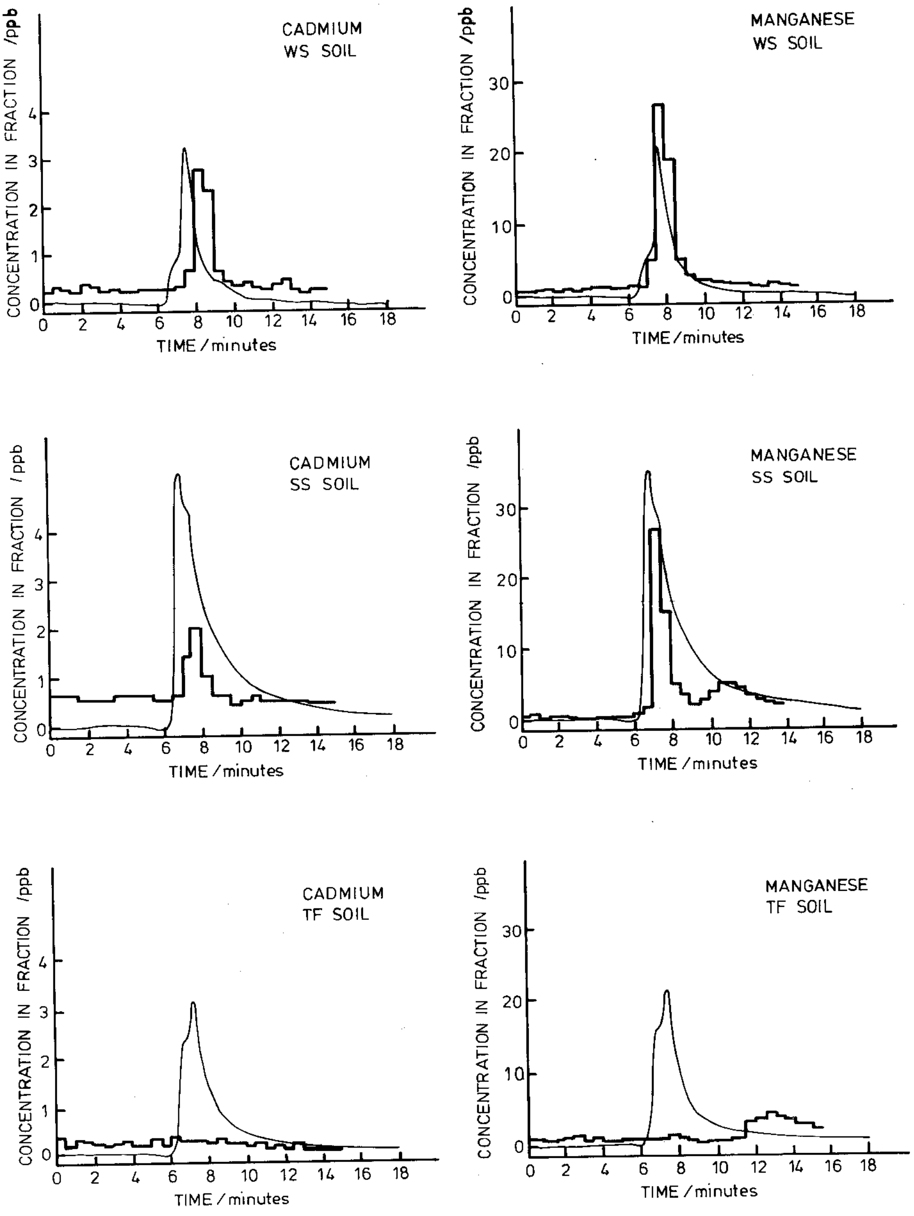

FIGURE 1 HPLC-GFAAS traces for cadmium and manganese showing UV detector response (——) and AAS response (——).

TABLE I

Some basic data on the soils studied

	WS	TF	SS	Sludge
Description	Typical brown earth	Grey rendzina	WS + 6.25% sludge	Soil sewage sludge
pH	7.0	6.9	7.4	—
Organic matter/%	4.0	4.3	5.3	40.0
Cation exchange capacity/meq $100\,g^{-1}$	9.8	31.3	—	—
Cadmium/ppm	1.8	1.8	2.3	29.9
Manganese/ppm	950	860	290	470
Sampled at:	Windscale, Cumbria	Harwell, Oxfordshire	—	Slough, Buckinghamshire

workers who conclude cadmium in soil-pore waters is present largely as $Cd(H_2O)_6^{2+}$.[6,7]

A quantitative difference was seen in the cadmium traces for WS and SS soils. The SS soil showed an increased UV response, corresponding to the increased organic material present. However the amount of cadmium in the fractions had approximately halved, despite the higher cadmium level in SS soil compared with WS soil. There are several factors that may be responsible for this. Firstly, the pH of the SS soil was higher by 0.4 pH units. A previous report[8] suggests that in sludged soil, a pH difference of several units would be required to account for the reduction by a factor of 2 in extractable cadmium. Secondly the increase in total organic matter present in the SS soil may have immobilised cadmium in the form of water insoluble complexes. Alternatively, by virtue of having grown crops on the SS soil for several growing seasons, the bulk of the water soluble cadmium may have already been taken up by the vegetation.

The behavior of manganese was somewhat different. The WS and TF soil-pore waters each only showed a single peak, eluting at different retention times. The SS soil-pore water showed both clearly resolved. The peak eluting in WS and SS soil-pore waters at 8 minutes, coeluted with most of the organic material, and eluted at the same time as a standard solution of Mn^{2+}. As with cadmium, we conclude that this is most probably due to the free hydrated metal ion. The second peak, observed in TF and SS soil-pore waters, was due to a species absorbing onto the column. The large excess of potassium and chloride ions should inhibit ionic species being absorbed, which may imply the species was a neutral complex containing manganese. The longer tails on the UV traces for TF and SS indicate retention of some organic material. Sposito,[9] using his GEOCHEM computer model, predicts the presence of Mn^{2+}, $MnSO_4$ and organomanganese complexes in soil solutions.

As with cadmium, no free metal ion was observed in solution from the TF soil. Again the relatively high cation exchange capacity would account for this, with manganese being bound in insoluble complexes. Quantitatively, the amount of extractable manganese in WS and SS soils was comparable, despite a much smaller amount of manganese in the SS soil itself. The reduced amount of manganese (and cadmium) in SS soil, relative to the amount that should be present based on mixing WS soil with sludge, is due to the SS soil having been used in a growing experiment lasting several seasons. The pots have all been subirrigated so that metals (and radionuclides) would not leach out. The reduction in manganese and cadmium is probably due therefore to uptake by the plants.

We have additionally attempted to perform the separations on gel permeation liquid chromatography columns, using some of the Sephadex and Sepharose range of gels (Pharmacia (UK) Ltd) but found problems associated with high background cadmium levels. The flow rates were also inconveniently slow. Flame AAS and ICP-OES have both been used as on-line detectors for our HPLC eluent, but the low levels of cadmium present in these pore-waters necessitated the use of GFAAS.

CONCLUSIONS

This work demonstrates that cadmium exists in the soil-pore waters of three soils in only one chemical form, thought to be the free hydrated metal ion. Manganese in the same soil-pore waters occurs in different forms. Despite comparable total cadmium and manganese concentrations in the soils themselves, the amount extracted in soil-pore water varies considerably. This is additional evidence that the two metals occur in various forms in these soils. The addition of sewage sludge to one of the soils increased the total cadmium content, but either reduced the amount of water soluble, and hence bioavailable, cadmium or enhanced the uptake of cadmium by vegetation. The addition of the sludge drastically altered the amount and form of the water soluble manganese in these soils.

We have demonstrated the potential of combined liquid chromatography-optical spectroscopy to produce data on speciation of trace metals in real environmental samples, rather than synthetic laboratory standards. The method has produced experimental data in accordance with published computer predictions based only on thermodynamic considerations.

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