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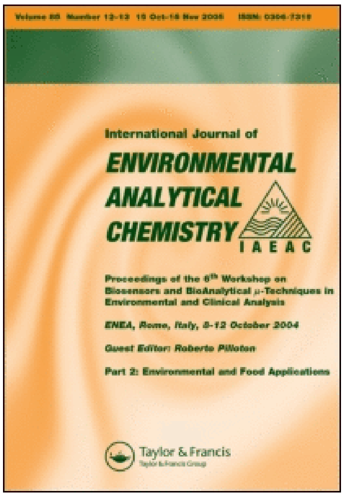

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SPECIATION OF HEAVY METALS IN SEWAGE SLUDGE AND SLUDGE-AMENDED SOIL

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The presence of heavy metals in sewage sludge restricts their agricultural use. Sequential extraction procedures may provide an assessment of the mobility of these elements in sludge and sludge-amended soil, and may help to predict the release of metals in soil solution. Nevertheless, the "phases" in which an element occurs are operationally defined and it is necessary to standardize a procedure in order to allow the comparison of results from different laboratories.

KEY WORDS: Heavy metals, sewage sludge, metal speciation, soil pollution.

INTRODUCTION

The heavy metal content of sewage sludge is the main factor which still restricts their agricultural use. The distribution of heavy metals in the different forms and phases in which they occur in soil and sludge can be determined using sequential extraction procedures [1-4]. The "forms" or "phases" are operationally defined by means of reagents and procedures used to isolate an element fraction.

Sequential extraction procedures provide information about the differentiation of the relative bounding strength of metals on various solid phases and about their potential reactivity under different physico-chemical environmental conditions.

Such extraction procedures make it possible to evaluate the mobility of metals in the environment; the metals associated with the "exchangeable" and "oxidizable" phases are, in fact, easily mobilized by ion exchange reactions and by the decomposition and transformation of organic matter. These techniques may help to predict the release of heavy metals in soil solution.

METHODS

In this work, a modified Tessier procedure [3], was used. The main difference with the method of Tessier is the extraction of the "oxidizable" phase after the extraction of the "exchangeable" phase. This method allows the destruction of organic matter which entraps the mineral materials and then provide a better extraction of the following phases.

Step 1 Exchangeable cations: $BaCl_2$ 1 mol/l, 16 ml, shaking during 2h.
Step 2 Oxidizable phases (organic fraction and sulphides): H_2O_2 8.8 mol/l + HNO_3 0.02 mol/l, (5 + 3), 16 ml, shaking during 5h + 1 h at 98°C; extraction with CH_3COONH_4 3.5 mol/l, 10 ml, shaking during 1 h.
Step 3 Acid-soluble phases (carbonates): CH_3 COOH 1 mol/l + CH_3COONa 0.6 mol/l, 35 ml, shaking during 5h.
Step 4 Reducible phases: (Fe and Mn oxihydrates): NH_2OH,HCl 0,1 mol/l, HCl + 4 mol/l CH_3COOH, 35 ml, 4h shaking + 1 h at 98°C: extraction with CH_3COONH_4 3.5 mol/l, 10 ml, shaking during 1 h.
Step 5 Residual fraction: dry ashing at 550°C during 2h + conc. HCl + HF (1 + 1), 20 ml, evaporation to dryness.

The concentrations of heavy metals in the extracts were measured by electrothermal atomic absorption spectrometry.

The aim of this work was to determine the distribution of heavy metals in the various component phases of sewage sludges, sampled at various stages of a treatment plant, and to investigate the mobility of cadmium and nickel by extracting them from the sludges as this mobility is critical for agricultural use.

The sludges investigated were taken from a sewage treatment plant, from the Bordeaux urban area, including liquid waste from a battery manufacturing plant. These sludges were characterized by a very high level of contamination by cadmium and nickel.

Besides, the migration and speciation of Cr, Pb, Ni and Cd were investigated in a sewage sludge-amended soil. The tests were carried out on samples from the INRA (Institut National de la Recherche Agronomique) experimental site at the Station d'Agronomie de Bordeaux, on which varying doses of sewage sludges containing a large amount of heavy metals, in particular Cd and Ni, has been spread. The sludge was anaerobically digested, conditioned by heat and dewatered using a filter-press. The soil was gravelly, with a very coarse texture. The following treatments were tested (beginning in 1976):

T: control, inorganic fertilization only,
A: application of 10 t ha^{-1} yr^{-1} (dry matter) of sludge until 1980.
B: application of 100 ha^{-1} $2yr^{-1}$ (dry matter) of sludge until 1980.

Since metals are generally associated with the fine fraction, the investigation was carried out on the fraction less then 125 µm of the of the samples taken in 1983.

RESULTS AND DISCUSSION

Mixed fresh sludge, anaerobic digested sludge, autoclaved sludge and filter dried sludge were investigated. Aerobic stabilization of mixed fresh sludge was carried out in the laboratory. Determination of the heavy metals dissolved in the pore water revealed that

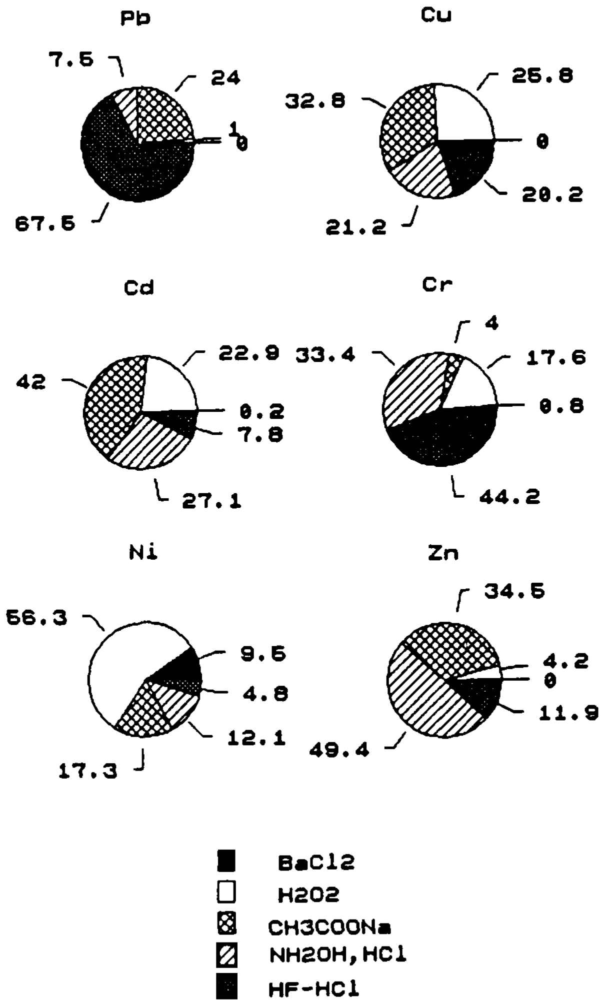

Figure 1 Speciation of metals in the anaerobic digested sludge. (% extracted).

nickel is the most soluble metal, while cadmium and lead are entirely associated with the solid phase of the sludges.

It was found that, during the sewage sludge treatment, the metals become less and less easy to mobilize, and tend to associate with the "reducible" and "residual" phases. Nevertheless, it seems that, in dried sludge that is to be discharged into the environment, all of the heavy metals except lead are potentially mobilizable, cadmium, and most of all nickel, being the most mobile since up to 25 % and 55 % of these metals appeared in the "exchangeable" and "oxidizable" phases.

The speciation of metals in the anaerobic digested sludge is presented in Figure 1; the complete results of this study are presented elsewhere [5].

The study of the migration and speciation of heavy metals was carried out on samples from a sewage sludge-amended soil taken in an experimental site [6].

Table 1 Sequential extraction of metals from sewage sludge-treated soils (% extracted, dry wt.) Treatment A, sludge 10 t/ha/yr 0 – 20 cm layer (1983)

	Exchangeable %	*Oxidizable* %	*Acid-sol.* %	*Reducible* %	*Residual* %	*Total* *mg/kg*
Cr	-	14.5	7.0	10.8	*67.7*	23.4
Pb	1.1	5.8	*55.2*	23.5	14.4	56.6
Ni	15.4	*53.8*	7.3	17.8	5.7	128.0
Cd	*65.1*	27.1	5.0	2.5	0.3	60.7

Treatment B, sludge 100 t/ha/2 yrs, 0–20 cm layer (1983).

	Exchangeable %	*Oxidizable* %	*Acid-sol.* %	*Reducible* %	*Residual* %	*Total* *mg/kg*
Cr	0.2	10.8	17.1	18	*53.9*	41.9
Pb	-	1.7	26.7	*55.7*	15.9	81.6
Ni	11.3	*46.1*	10.4	15.6	16.6	492.0
Cd	*36.1*	18.0	34.3	11.3	0.3	216.0

The concentration of metals measured in this way shows a large increase in the metal contents of the surface horizon. It can be seen that there are large increase of Cd down to the 60–80 cm layer and of Ni down to the 40–60 cm layer in the case of massive applications of sludge. In the system studied and over the time period concerned (1976–1983), the following observations have been made (Table 1).

Among the four metals studied, Cd is the one that migrates most readily in the soil, down to the 60–80 cm layer. Most of the Cd is in an "exchangeable" form in the soil (i.e. extracted by $BaCl_2$ in this case), and this relative ease of exchange must be considered in the light of both the great mobility of this metal in soil horizons which was demonstrated and the uptake of Cd by plants.

Ni is associated primarily with the "oxidizable" phase, and migrated down to the 40–60 cm layer.

Pb is associated with the "acid-soluble" and "reducible phase" and did not display a great mobility in the soil, i.e. not farther than the 20–40 cm layer.

The additions of Cr were smaller and this metal remains localized in the upper layer. Cr is found primarily in the residual phase.

It is therefore assumed that the spreading of sewage sludges containing large quantities of heavy metals may contaminate sandy soils down to deep layers, especially in the case of Cd. Moreover, the method of selective extractions provides information about how the metals are bound to the soil, and may therefore help to predict their mobility.

CONCLUSION

Single extraction techniques, and moreover sequential extraction procedures provide information about the way metals are bound to sludge and soil, and may therefore help to predict their mobility. The metals associated with the "exchangeable" and "oxidizable" phases are easily mobilized by ion exchange reactions and by the transformation of organic matter.

On sludge treated soils we can achieve an assessment of the mobility of metals by adding the percentage of metals present in these phases. In contrast, the metals associated with the "residual" phase are not able to be released and may constitute the background level of metals in soil.

However, it has been shown that an important redistribution of trace elements among phases may occurs during the extraction procedure [7] and that the comparison between various extraction techniques is difficult, moreover, an uncertainty on the significance of the extracted metal remains [8].

Consequently, it is necessary to define a reference method for the sequential extraction of metals and to validate this method in relation to the mobility and availability of metals in the environment.

References

1. A. Tessier, P.G.C. Campbell and M. Bisson, *Anal. Chem.*, **51**, 844–851 (1979).
2. U. Forstner, W. Calmano, K. Conradt, H. Jaksch, C. Schimkus, and J. Schoer, *Proc. Intern. Conf. Heavy Metals in the Environment, Amsterdam*, (C.E.P. Consultants Ltd, Edinburgh, 1981), pp. 698–704.
3. N. Meguellati, Mise au point d'un schéma d'extractions sélectives des polluants metalliques associés aux diverses phases constitutives des sédiments, Thèse 3ème cycle, Université de Pau, (1982).
4. M. Legret, D. Demare, and P. Marchandise, *Proc. Intern. Conf. Heavy Metals in the Environment, Heidelberg*, (C.E.P. Consultants Ltd, Edinburgh, 1983), pp. 350–353.
5. M. Legret, L. Divet, and P. Marchandise, *Water Res.*, **5**, 541–547 (1987).
6. M. Legret, L. Divet, and C. Juste, *Water Res.* **8**, 953–959 (1988).
7. D. Robbe, *Proc. Intern. Conf. Heavy Metals in the Environment, New Orleans*, (C.E.P. Consultants Ltd, Edinburgh, 1987), pp. 360–362.
8. P.W.W. Kirk, D.L. Lake, J.N. Lester, T. Rudd, and R.M. Sterrit, *Water Research Center Report Environment TR 226* (Ed. J.A. Campbell, Medmenham, 1985), 70 p.