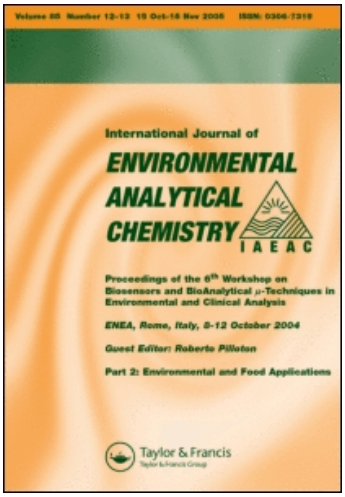

International Journal of Environmental Analytical Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Sequential Extraction of Copper and Zinc from Sewage Sludges. Use of Organic Solvents

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To cite this Article Vieira, J. M. , Silva, e. , Domingues, H. and Mesquita, Ma E.(1993) 'Sequential Extraction of Copper and Zinc from Sewage Sludges. Use of Organic Solvents', International Journal of Environmental Analytical Chemistry, 51: 1, 109 — 112

To link to this Article: DOI: 10.1080/03067319308027615

URL: http://dx.doi.org/10.1080/03067319308027615

Intern. J. Environ. Anal. Chem., Vol. 51, pp. 109-112
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SEQUENTIAL EXTRACTION OF COPPER AND ZINC FROM SEWAGE SLUDGES. USE OF ORGANIC SOLVENTS

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(Received in final form, 31 August 1992)

Sequential extraction procedures were used to evaluate the bioavailability of metals from two sewage sludges after application in soils. Organic solvents were used prior to sequential extraction to evaluate the influence of oil and waxes on heavy metals extractability.

The preliminary results showed that a extraction of oil and waxes present in the sewage sludges by n-hexane followed by acetone increased the accessibility of Cu and Zn and did not remove substantial metal amounts.

KEY WORDS: Sewage sludges, oil, copper, zinc, sequential extraction.

INTRODUCTION

Sewage sludges often contains high levels of heavy metals that are harmful to the environment. Sewage sludges from Portuguese plants do not yet present very high contents of heavy metals, but the development of the country will promote increasing amounts of high levels heavy metals sludges that may constitute environmental damage.

In order to control this problem, it is necessary to evaluate heavy metals mobility within the soil and to determine their chemical associations with the soil materials. Sequential extraction techniques may be a good compromise for assessing the bounding states of heavy metals by using a variety of chemical reagents. The extractable contents are often referred to "phases" (*e.g.* exchangeable, organic, oxides, sulfides) by many authors[1,2] although these determinations are operationally defined[3].

Our aims were to determine, in a preliminary study, the copper and zinc distribution on the different fractions of sewage sludges, before and after treatment with organic solvent, in order to evaluate the removal of metals dissolved by aqueous extractants and to understand what might happen in the near future after the agricultural use of the sludges.

MATERIAL AND METHODS

Two sewage sludges samples from Elvas and Évora plants were collected, dried and finely ground in a agate mill (0.074 mm) before storage. The total heavy metal contents were extracted by triacid attack (HNO_3, HF, $HClO_4$). Oil and/or waxes were removed[2] from subsamples (5 g) of each sludge by n-hexane (10 ml) followed by acetone (10 ml) extraction. The material was shaken and centrifuged after each application.

Duplicate samples (1 g) of the sewage sludges were submitted to sequential extraction, before and after treatment with organic solvents, being separated into five fractions: exchangeable — 40 mL of 0.5 M $Ca(NO_3)_2$[4], 16 hours; acid-soluble — 40 mL 0.44 M acetic acid[4], 8 hours; easily reducible — 0.1 M hydroxylamine hydrochloride[5], shaken 30 minutes; organic — 0.1 M $K_4P_2O_7$[4], 24 hours; Fe-oxides/hydroxides — 0.2 M ammonium oxalate, 0.2 M oxalic acid (pH 3.0) and 0.1 M ascorbic acid[5], 80°C, 30 minutes.

Extractions were carried out at laboratory temperatures (20° ± 2°C). Samples were washed between extractions with 0.025 M $Ca(NO_3)_2$ to remove occluded solutions. Metals were determined by routine procedure in the centrifuged solutions by air- -acetylene flame atomic absorption spectrophotometry. Calibrant solutions for each element were made up with the appropriated extracting solutions and with each batch of extractions a blank sample was carried out.

RESULTS AND DISCUSSION

The metals present in the sewage sludge samples are mainly Zn, Cu, Fe and Pb in different levels according to plant localization (Table 1). Elvas sludge presents less Cu (275 mg kg^{-1}) and more Zn (2575 mg kg^{-1}) than Évora sludge (Cu — 626 mg Kg^{-1}; Zn — 913 mg kg^{-1}). Sludge from Elvas plant presents zinc level higher than the minimum limit (2500 mg kg^{-1}) suggested by E.C. Directive.

Comparing the results of total Cu, Zn and Fe (Table 1) with the sum of the elements removed by sequential extraction (Tables 2 and 3) we can conclude that Elvas sludge presents higher metal contents within silicate mineral structures (residual fraction) than the one from Évora.

Results of sludge sequential extractions (Tables 2 and 3), obtained either with or without organic solvents, showed that the organic solvent did not remove substantial metal amounts, but the distribution of the metals in the fractions of both sewage sludges was different. So, after treatment with the solvent, Cu associated to organic matter and Fe oxides/hydroxides was displaced and was distributed on "phases" exchangeable, acid-soluble and easily

Table 1 Chemical characteristics of sewage sludges (total analysis mg kg^{-1}).

Elements	*Cu*	*Fe*	*Zn*	*Cr*	*Ni*	*Pb*	*Cd*
Sample 1 (Elvas)	275	15550	2575	74	48	520	4.0
Sample 2 (Évora)	626	9360	913	51	59	153	3.5

Table 2 Metal sequential extractions on sewage sludges, without organic solvent.

	Sample 1 (Elvas) (mg kg^{-1})			*Sample 2 (Évora) (mg kg^{-1})*		
Extractions	*Cu*	*Zn*	*Fe*	*Cu*	*Zn*	*Fe*
exchangeable	9	83	12	33	55	12
acid-soluble	10	700	21	68	410	25
easily reducible	0.4	46	10	2	17	10
organic matter	60	366	3500	150	104	2680
Fe-oxides/hydrox.	90	92	7700	235	33	5500
Total	169	1287	11243	488	620	8227

reducible; the Zn associated to organic matter was displaced and distributed on "phases" exchangeable, acid-soluble and easily reducible. The Fe was displaced, mainly, from organic and Fe-oxides to easily reducible fraction.

CONCLUSIONS

From the results in both extraction procedures with and without oil and waxes we may conclude that the sequential extraction scheme used in this work presented differences among metal distribution on sewage sludge fractions, meaning different metal availability. Copper associated to Fe-oxides/hydroxides and organic matter was more easily displaced after treatment with n-hexane-acetone and was measured on exchangeable, acid-soluble and easily reducible sludges fractions. Zinc adsorbed on Fe-oxides/hydroxides was not affected by organic solvents; this metal present on organic matter fraction was displaced after treatment and measured on exchangeable, acid-soluble and easily reducible sludges fractions.

These results showed that in environmental pollution studies is very important to know the speciation of the heavy metals in both sewage sludges with and without oil and waxes, to understand the mechanisms of trace elements transport in the agricultural land with sewage sludge. It is also important to take into account the reagent selectivity in sewage sludge and soil sludge amended.

The use of organic solvents in sewage sludge was complicated due to their quick evaporation. Further work in this subject is necessary to improve the analytical techniques.

Table 3 Metal sequential extractions on sewage sludges, with organic solvent.

	Sample 1 (Elvas) (mg kg^{-1})			*Sample 2 (Évora) (mg kg^{-1})*		
Extractions	*Cu*	*Zn*	*Fe*	*Cu*	*Zn*	*Fe*
exchangeable	12	137	13	41	52	12
acid-soluble	16	850	22	102	460	30
easily reducible	38	350	650	170	54	720
organic matter	47	62	4850	75	17	3000
Fe-oxides/hydrox.	54	84	5200	96	29	3800
Total	167	1483	10735	484	611	7562

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