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Evaluation for Agricultural Usage with Speciation of Heavy Metals in a Municipal Sewage Sludge

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Abstract This study was carried out to evaluate the agricultural usage of an anaerobically digested sludge in the contents and fractions of heavy metals. Therefore, a sequential extraction scheme according to the BCR's (Community Bureau of Reference) guidelines and total acid digestion were applied to sewage sludge samples. The results of total heavy metal concentrations in sewage sludge showed that the highest total concentrations were Fe, Zn and Mn. When Turkish, Europe and US EPA directives were compared with each other by depending on the use of sludge for agricultural purposes, all the heavy metals determined for this sludge were below the maximum permitted levels, except for Cd. This sludge should not be applied to land due to its high Cd content. The results of heavy metal fractions indicated that some metals (Cd, Mn, Pb, and Fe) distributed mainly in the residual fraction. All fractions of Zn showed no variation. Cu and Cr were most abundant in the oxidizable phase while Ni was in exchangeable phase. Although total content of Ni in the sludge is lower than the maximum levels allowed by all the directives, it tends to be easily moved and dispersed in the environment. Due to its high mobility, the examined sewage sludge may cause phyto-toxicity after its agricultural application.

Keywords Sequential chemical extraction · Heavy metals · Sewage sludge · Community Bureau of Reference

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The production of sewage sludge has increased gradually in the worldwide due to the demand for better quality water and the more strict environmental laws recently (Walter et al. 2006). The basic disposal methods for large quantities of sludge are land application, landfilling, incineration, ocean dumping and lagooning (Babel and Dacera 2006). Among the different ways of sewage sludge disposal, the land application used widely has a low cost and a high effect (Mossakowska et al. 1998). Usage of sewage sludge as fertilizer or as soil amendment seems an attractive possibility due to their potential values of organic matter, N, P and other plant nutrients that can improve the physical and biological properties of the soil (Zufiaurre et al. 1998; Fuentes et al. 2004; Fuentes et al. 2006; Walter et al. 2006; Wang et al. 2006). However, sewage sludge contains many organic contaminants such as PCB and PAHs, heavy metals and pathogens. The conventional treatment of sewage sludge can degrade the parts of the organic pollutants and kill effectively some pathogens, but heavy metals present in sludge cannot be removed by these treatment technologies such as composting, aerobic or anaerobic digestion. Therefore, the land application of sludge after a conventional treatment method creates a potential problem regarded to public health if the toxic metals present in the sludge move from soil to plants or transport to groundwater by drainage way. The metal content of sludge varies by depending on wastewater characterization. It was reported that the total heavy metal content of sewage sludge varied in the range of 0.5–2% on a dry weight basis and in some cases increased up to 4% on a wet weight basis, especially for metals such as cadmium(Cd), chromium (Cr), copper (Cu), nickel(Ni), lead (Pb) and zinc (Zn) (Babel and Dacera 2006). The studies on heavy metal concentrations in sewage sludge and their bioavailability have received a great scientific attention in recent years, because it is necessary to get the detailed information about heavy metals present in sewage before their land application (Wang et al. 2005).

The total metal concentration obtained after a strong acid digestion does not provide sufficient information of its potential hazardous effects on environment because the mobility and eco-toxicity of heavy metals depend strongly on their specific chemical forms or binding. Consequently, these are the parameters that have to be determined, rather than the total element contents, in order to assess toxic effects (Fuentes et al. 2004; Wang et al. 2006). If heavy metals exist as loosely bound fractions such as soluble, exchangeable and adsorbed forms, they tend to be easily moved and dispersed. However, metals asscoiated with organic ligands or in crystal lattices are not easily separated or mobilized. To determine the speciations of heavy metals, various methods have been developed over the last two decades involving both single and sequential extraction schemes (Alonso Alvarez et al. 2002). Although some methods have been widely used, none has been unreservedly accepted by the scientific community. For this reason the Community Bureau of Reference (BCR) in 1987 began a programme to harmonise the methodology in the sequential extraction schemes used for determining metals in a variety of matrices, including lake, lagoon and marine sediments, sewage sludge, soil and industrially contaminated made-up ground (Sahuquillo et al. 1999; Fuentes et al. 2004). The aim of this study was to determine total heavy metals contents and their chemical fractions in the anaerobically digested sewage sludge. Thus, the data obtained in detail by BCR method can be used to evaluate both metal mobility and bioavailability and suitability of the sludge disposal for land application.

Materials and Methods

Anaerobically stabilized sludge was obtained from a wastewater treatment plant located in the province of Kayseri, Turkey. The wastewater treatment plant processes both industrial and domestic effluent corresponding to 800,000 person equivalents per day. This plant is operated as conventional active sludge process and extended aeration system. Sewage sludge generated are digested anaeorbically and then dewatered mechanically. Firstly, the samples were air-dried and then dried at 55°C in the oven for total element analysis. The samples were then ground and sieved to obtain a fraction of less than 150 mesh. The resulting material was stored in dry glass bottles at room temperature until analysis. All treatments were done in duplicate.

Physicochemical properties of the sludge sample were determined according to different parameters such as pH and electrical conductivity (EC). Sludge pH and EC were measured in 1:10 sludge and water suspensions using a pH and conductivity meter, respectively (Wang et al. 2006). The macroelements of calcium, potassium and sodium were totally determined by flame photometry (Jenway PFP 7), and magnesium was also totally determined by atomic absorption spectrometry (UNICAM 929).

Total heavy metal concentration was determined by AAS after digestion of the samples with microwave assisstance. 0.25 g dry sludge (<150 mesh) was weighted in a PTFE digestion vessel and 7 mL HNO_3 (65% w/w), 2 mL HF (40% w/w) and 1 mL $HClO_4$ (60% w/w) were added. The digestion vessel was placed in the chamber of the microwave system (Milestone Ethos D). After digestion, the sample solution was allowed to air-cool and then diluted with deionized water to 50 mL.

The sequential extraction was performed using the three-step procedure recommended by BCR. The method details are presented in Table 1. In the step 2, an increased concentration of $NH_2OH.HCl$ and lower pH were applied as recommended by Mossop and Davidson (2003) to improve reproducibility due to a more efficient dissolution of the reducible fraction of the sludge.

Step 1

A 40 mL volume of 0.11 M acetic acid was added to 1 g of dried sewage sludge. The mixture was shaken for 16 h at room temperature (approx. 21°C) on a mechanic shaker. The extract was separated from the solid residue by centrifugation at 1,200 rpm. The liquid was stored at 4°C before analysis. The residue was washed with 20 mL distilled water by shaking for 15 min, centrifuged and the washings discarded.

Table 1 Sequential extraction procedures

Step	Fraction	Target phases	Modified BCR
1	Exchangeable, water and acid soluble	Soluble species, carbonates, cation exchange sites	0.11 mol L-1 acetic acid
2	Reducible	Iron and manganese oxyhydroxides	0.5 mol L-1 hydroxylammonium chloride at pH 1.5
3	Oxidisable	Organic matter and sulphides	Hydrogen peroxide followed by 1.0 mol L-1 ammonium acetate at pH 2
4	Residual		7 mL HNO_3 + 2 mL HF + 1 mL $HClO_4$

Step 2

A 40 mL aliquot of 0.5 M hydroxylamine hydrochloride (adjusted to pH 1.5 with HNO_3) was added to residue from Step 1. The extraction procedure was repeated as described in Step 1.

Step 3

A 10 mL aliquot of 8.8 M hydrogen peroxide was added in small amounts to avoid violent reaction to the residue from Step 2. The mixture was digested at room temperature for 1 h with occasional shaking. Digestion was continued at 85°C in a water bath for 1 h. The mixture was reduced to a small volume (1–2 mL) by further heating. A second 10 mL aliquot of H_2O_2 was added and the digestion continued at 85°C for 1 h. The volume reduction was repeated. Then, 50 mL of ammonium acetate (adjusted to pH 2 with nitric acid) was added and the extraction was performed as above.

Step 4

The material remaining in the end of the BCR procedure was digested for determining total metal concentration.

The concentrations of Cd, Cr, Pb, Cu, Ni and Zn in different fractions and the resultant solutions of Step 4 were determined by AAS.

Results and Discussion

Table 2 shows some physicochemical properties of the sludge studied. The pH value and the electrical conductivity (EC) of the sludge were 6.32 and 4.97 mS cm^{-1}, respectively. The EC of the sludge was high, which means a high salt content. Among the cationic macroelements, magnesium was the most abundant, followed by sodium, calcium and potassium.

The investigation of heavy metal concentrations in sewage sludge is important and necessary for interpreting their potentials in agricultural usage. Total concentrations of various heavy metals obtained after the digestion with microwave assistance were compared with the limits allowed by the Guide of Soil Pollution of Turkey, Europe and US EPA (Table 3).

Table 2 Physicochemical properties of the sludge

Parameters	Anaerobic sewage sludge
PH	6.32
EC	4.97
Ca (mg kg^{-1})	19.696
Mg (mg kg^{-1})	45.200
Na (mg kg^{-1})	23.430
K (mg kg^{-1})	13.000

Fe, Zn and Mn were the predominant metals in the sludge. All the heavy metals values determined were below the maximum values allowed in the directives, except for Cd. The total concentration of Cd was very high. It is very important to consider that this element has high toxicity, thus it restricts the agricultural use of the sludge due to the potential risk of soil contamination (Fuentes et al. 2004). The content of Co in the sludge was below the detection limit of AAS. Therefore, we did not take into consideration.

The concentration of exchangeable, reducible, oxidizable and residual metals obtained after the application of the sequential extraction recommended by the BCR and the recovery rate were represented in Table 4. The percentages of species of heavy metals in the total contents were also illustrated in Fig. 1. The sum of extractable fraction of metals is reasonably similar to total contents obtained after the digestion with microwave assistance. The recovery rate was 65.1–106.4%, which was similar to those performed the same extraction scheme by Fuentes et al. 2004 and Wang et al. 2006.

Cd distributed principally in the residual fraction. In a previous study, the residual fraction for Cd was predominant (Wang et al. 2005). The oxidizable fraction for Cr was determined as the predominant, which is similar to the data published by Alonso Alvarez et al. 2002. Cu was found significantly in the oxidisable fraction, which is similar to results from some previous studies (Fuentes et al. 2006; Walter et al. 2006). This form exhibits a significant degree of availability and mobility. Mn was predominant in residual and oxidizable fraction. Some researchers found Pb to be principally distributed between oxidizable and residual fraction (Wang et al. 2005, 2006). Our results

Table 3 Total concentrations (mg kg^{-1}, dry weight) of heavy metals in the sludge and their allowed values in the guide of soil pollution of Turkey

Heavy metals	Anaerobic sewage sludge	Turkey	Europe	US EPA
Cd	242	40	20–40	39
Cr	598	1200	–	–
Pb	286	1200	75–1200	300
Ni	248	400	300–400	420
Zn	1848	4000	2500–4000	2800
Cu	652	1750	1000–1750	1500
Mn	976	–	–	–
Fe	22.700	–	–	–
Co	ND	–	–	–

Table 4 Metal concentration (mg kg^{-1}) of extractable fraction for the anaerobically digested sewage sludge

Heavy metals	Exchangeable	Reducible	Oxidizable	Residual	Sum	Total concentration	Recovered %
Cd	24.4	43.2	0.48	165	233.1	242	96.3
Cr	16.8	52.4	440	20.3	529.5	598	88.5
Cu	92.3	151.2	265.6	120.7	629.8	652	96.6
Mn	160	24	303.8	550.6	1038.4	976	106.4
Pb	0.50	80.1	0	105.6	186.2	286	65.1

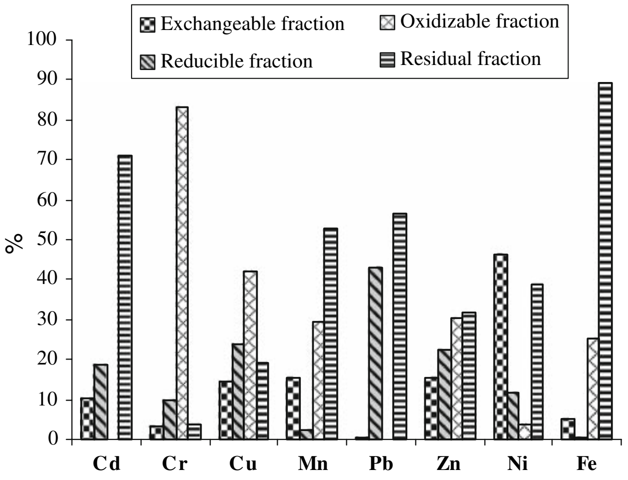

Fig. 1 The percentage of metal fractions of the heavy metals in their total contents

were slightly similar to results from these researches. The oxidizable fraction was below the detection limit while the residual fraction of Pb was the highest. Zn distributed mainly as the residual and oxidizable fraction in our study. On the other hand, some researhers reported Zn was dominant in the reducible fraction, followed by the oxidizable (Walter et al. 2006; Wang et al. 2006). This difference might be due to the properties of the sludge and the sources of heavy metals. Additionally, the sludge pH might have affected the distribution of metal fraction in sludge (Wang et al. 2006).

The Ni concentration was highest in the first fraction. This agrees with some previous results that Ni in the anaerobic sewage sludge was in the exchangeable fraction (Alonso Alvarez et al. 2002; Walter et al. 2006). For Fe, the predominant fraction was the residual, which was consistent with the findings by Wang et al. 2006 and Fuentes et al. 2006.

Conclusion

In order to evaluate the agricultural usage of sludge analysed, total heavy metals contents and their fractions were investigated. The results in total heavy metal concentrations of sewage sludge showed that the highest concentrations were Fe, Zn and Mn. Except for Cd, all the total concentrations were below the maximum values allowed in the directives of Turkish, Europe and US EPA. The high Cd hinders the application of this sludge to agricultural lands.

The results obtained after the application of the sequential extraction recommended by the BCR indicated that Cd, Mn, Pb, and Fe distributed mainly in the residual fraction that means almost inert. Cu and Cr were most abundant in the oxidizable phase while Ni was in exchangeable phase. Although total content of Ni in the sludge was lower than the maximum level allowed by all the directives, it could easily move and disperse in the environment because of its exchangeable form. The mobility and bioavailability of Ni in sludge may cause phyto-toxicity after its agricultural application. Therefore, the rate of sludge application and the heavy metals having high levels in exchangeable and reducible forms such as Pb and Ni, should be taken into account.

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