Original Paper

Identification of Chemical Forms of Lead, Cadmium and Nickel in Sewage Sludge of Waste Water Treatment Facilities

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Abstract. Lead, cadmium and nickel levels in sewage sludge of a waste water treatment facility were determined by slotted tube atom trap (STAT)-flame atomic absorption spectrometry after using different extraction reagents. In addition, a sequential extraction procedure was applied to the same samples and the results were compared. It was found that Pb and Cd were relatively mobile as organically bound, carbonate or adsorbed on the Fe–Mn oxides and the concentrations in the extracts were higher than 50%. However, the percentage of Ni bound to these phases was found to be very low.

Key words: Cadmium; lead; nickel; sewage sludge; AAS; speciation.

Domestic effluents probably constitute the largest single source of elevated metal concentrations in rivers and lakes. Sewage sludge, especially from industrial or mixed areas, contains elements in concentrations that cause direct or indirect symptoms of toxicity to vegetation. The identification of the chemical form of trace metals in soil is necessary for estimating their biological availability, physico-chemical reactivity and transport in the environment and into the food chain.

In one broad definition of speciation [1], the species are defined by their function, as, for example, 'plant available forms', 'exchangeable cations' or 'labile species'. In unpolluted soils, trace metals are mainly bound to silicates and primary minerals forming relatively immobile species, whereas in polluted ones trace metals are generally more mobile and bound to other soil phases. The determination of the different kinds of binding gives more information on trace metal mobility, as well as on their availability or toxicity, than the total element content. But the determination of these different kinds is difficult and often impossible. The general approach has been to separate the soil into different fractions and, by analysing each fraction, to determine the amount of element combined or associated with each soil fraction or phase. Alternatively, the fractionation may be performed by extraction of the soil with chemical reagents or solvents designed to extract the elements bound in, or associated with, a particular soil phase or component [2–4]. Although their precise chemical form may be indeterminate, the function is quite precise. This kind of speciation has, for half a century, been a major activity in soil and agricultural laboratories. Because of the poorly specific nature of most single extractants, sequential extraction procedures have been devised to limit the access of an extracting reagent to no more than a single specific soil phase [5]. Sequential extraction procedures designed to isolate a number of soil phases, while offering a considerable improvement in phase-specificity, are still not perfect and both, tedious and difficult to use.

The possible carcinogenic effect of Cd [6], the highly toxic and cumulative poison Pb [7], and the allergenic and in some of its compounds even carcinogenic effect of Ni [8] have drawn attention to the determination of these metals in environmental samples. They may enter the organism via the alimentary and/or respiratory tract, so the main non-occupational sources of this metal are food, drinking water and air [9]. These metals in sewage sludge are very likely in organic chelated or other mobile forms and thus, readily available to plants. Use of the sewage sludge as fertiliser is a serious risk because these metals in sewage sludge may leach into groundwater or be taken up by plants and enter the food chain.

Although electrothermal atomization atomic absorption spectrometry (ETA-AAS) has been used successfully for the determination of these metals in soil, environmental, food and biological samples, sampling difficulties and high matrix salt levels can become an important source of errors [10, 11]. In the past two decades, many attempts have been made to reduce interferences in graphite furnace, including improved furnace and platform design and, particularly, use of effective chemical modifiers [12]. As a result, there is a tendency for improving the sensitivity in flame atomic absorption spectrometry (FAAS). The slotted tube atom trap (STAT) system was used for some elements, particularly for lead and cadmium [13, 14].

In this study, selective and sequential extractions were applied to sewage sludge samples for the speciation of cadmium, lead and nickel. Metal determinations were carried out by STAT-FAAS.

Experimental

Apparatus and Reagents

An ATI UNICAM 929 Model flame atomic absorption spectrophotometer (AAS) equipped with deuterium lamp background correction and with ATI UNICAM hollow cathode lamps was used for the determinations. The optimum conditions for FAAS were given in Table 1. A slotted tube atom trap (STAT) was used to increase the sensitivity of FAAS in the determination of Pb and Cd. In the extraction and digestion procedure, Snijders magnetic stirrer with heater, and a Hettich EBA III centrifuge were used.

Unless stated otherwise, all chemicals used were of high-purity reagent grade. Throughout all analytical work, doubly distilled water was used. All glass apparatus have been kept permanently full of $1 \, mol \, L^{-1}$ nitric acid when not in use. In the digestion and

Table 1. Operating parameters for FAAS

Parameter	Pb	Ni	Cd
Wavelength, nm	217.0	232.0	228.8
HCl current, mA	9.5	14.5	7.5
Acetylene flow rate, L/min	0.5	0.5	0.5
Air flow rate, L/min	4.0	4.0	4.0
Slit, nm	0.5	0.2	0.5

extraction procedures, concentrated nitric acid (65%, Merck), hydrogen peroxide (35%, Merck), $CaCl_2$ (Merck), KNO_3 (Merck), sodium acetate (Merck), ethylenediaminetetraacetic acid disodium salt (Na_2EDTA, Merck) hydroxylamine hydrochloride ($NH_2OH \cdot HCl$, Merck), sodium pyrophosphate ($Na_4P_2O_7$, Merck) and acetic acid (96%, Merck) were used. Stock solutions of cadmium, lead and nickel ($1000 \, mg \, L^{-1}$) were prepared by dissolving their nitrate salts in $1.0 \, mol \, L^{-1}$ nitric acid. A solution of 1% m/v $LaCl_3$ was used as the STAT coating material. This solution was sprayed on STAT when the flame of AAS was burning. So, the destruction of STAT by alkaline and earth-alkaline elements (especially, some compounds of these elements were used as solutions for extraction in this study) was delayed.

Digestion and Selective Extraction of the Sewage Sludge

The sewage sludge investigated was obtained from the Elazig-city treatment facility. Elazig-city in the east of Turkey has a population of about 250000 people. 4 ml of a mixture of nitric acid–hydrogen peroxide $(2 + 1)$ were added to the sewage sludge samples of 1.0 g and dried with occasionally shaking on a hot plate. After cooling, 4 ml of $1.5 \, mol \, L^{-1}$ nitric acid were added to the remainder and centrifuged. The clear digests were analysed by using direct STAT-FAAS for Pb and Cd and FAAS for Ni. A blank digest was carried out in the same way.

The sewage sludge extracts were obtained by, separately, shaking the sewage sludge samples of 1.0 g with 4.0 ml of following reagents. $1 \, mol \, L^{-1}$ $CaCl_2$, $1 \, mol \, L^{-1}$ KNO_3, $1 \, mol \, L^{-1}$ sodium acetate and $1 \, mol \, L^{-1}$ ammonium acetate were used for the exchangeable and weakly adsorbed fraction. 0.04 and $1.0 \, mol \, L^{-1}$ $NH_2OH \cdot HCl$ for fractions bound to Fe and Mn oxides, $0.1 \, mol \, L^{-1}$ Na_2EDTA for organically and carbonate bound, 1.0 and $0.5 \, mol \, L^{-1}$ acetic acid for the carbonate and exchangeable fractions, $0.2 \, mol \, L^{-1}$ sodium pyrophosphate ($Na_4P_2O_7$) for organically bound and acetic acid–acetate buffer solution of $pH = 5.0$ for carbonate fraction were used. The mixtures were shaken in the tube by vortex for 10 min and centrifuged. The clear digests were analysed by using direct STAT-FAAS for Pb and Cd and FAAS for Ni. The blank digests were treated in the same way.

Sequential Extraction

Three sequential extraction procedures were studied as described below. In each step, the mixture was shaken in the tube by vortex for 10 min. After centrifugation, the clear solution was analysed.

First sequential extraction procedure modified from Miller and McFee [15]

$1\,mol\,L^{-1}$ KNO_3 for exchangeable species

↓

$0.2\,mol\,L^{-1}$ $Na_4P_2O_7$ for organically bound species

↓

$0.1\,mol\,L^{-1}$ Na_2EDTA for carbonate species

↓

$1\,mol\,L^{-1}$ $NH_2OH \cdot HCl$ for adsorbed species on Fe and Mn oxides

↓

Concentrated HNO_3/H_2O_2 for residual species (except silicates)

Second sequential extraction procedure modified from Tessier et al. [16]

$1\,mol\,L^{-1}$ $CaCl_2$ for exchangeable species

↓

Acetic acid−acetate buffer (pH = 5.0)   for carbonate species

↓

$0.04\,mol\,L^{-1}$ $NH_2OH \cdot HCl$ for adsorbed species on Fe and Mn oxides

↓

Concentrated HNO_3/H_2O_2 for residual species (except silicates)

Third sequential extraction procedure modified from Tessier et al.[16]

$1\,mol\,L^{-1}$ $NaCH_3COO$ for exchangeable species

↓

Acetic acid−acetate buffer (pH = 5.0)   for carbonate species

↓

$0.04\,mol\,L^{-1}$ $NH_2OH \cdot HCl$ for adsorbed species on Fe and Mn oxides

↓

Concentrated HNO_3/H_2O_2 for residual species (except silicates)

Results and Discussion

To obtain the metal concentrations in various extraction solutions of the sewage sludge, the calibration curves were prepared as follows. For Pb and Cd, absorbances of the lead solutions of 0.1; 0.2; 0.4; 0.8; 1.5 mg L^{-1} and the cadmium solutions of 10, 20, 40, 80, 150 μg L^{-1} were measured by means of STAT-FAAS. The nickel solutions of 0.25, 0.5, 1.0, 2.0, 4.0 and 5.0 mg L^{-1} were measured by FAAS. The graphs obtained were rectilinear in the concentration ranges as described above and the equations of the curves were as follow:

$Y = 66.2\,X + 0.8$ $R^2 = 0.99$ for Pb X in mg L^{-1}

$Y = 0.40\,X + 0.33$ $R^2 = 0.99$ for Cd X in μg L^{-1}

$Y = 42\,X + 1.1$ $R^2 = 0.99$ for Ni X in mg L^{-1}

The results obtained by using selective and sequential extraction procedures are given in Tables 2–5. The values are the means of three completely independent digestions of the same sample.

Lead and Cadmium in Sewage Sludge

The behaviour of Pb and Cd are similar. Therefore, these elements were evaluated together. The solutions of $1\,mol\,L^{-1}$ $CaCl_2$, KNO_3, sodium acetate and ammonium acetate were used as reagents for the determination of exchangeable metal species. According to literature data [5], the exchangeable species that are weakly bound, electrostatically, are released from the matrix by aid of the cations in these reagents. From the results of Table 2 and Figs. 1 and 2, lead and

Table 2. Results of Pb, Cd and Ni contents in the sewage sludge samples by using different selective extracts (as mg kg^{-1} based on dried weight), $n = 3$

Extraction reagent	Pb	Cd	Ni
HNO$_3$/H$_2$O$_2$	22.2 ± 1.5	1.1 ± 0.01	39.5 ± 3
0.1 mol L^{-1} Na$_2$EDTA	12 ± 0.8	0.4 ± 0.04	6.0 ± 0.4
1 mol L^{-1} NH$_2$OH · HCl in acetic acid (25%)	5.0 ± 0.3	0.56 ± 0.05	1.8 ± 0.13
0.04 mol L^{-1} NH$_2$OH · HCl in acetic acid (25%)	2.6 ± 0.17	0.4 ± 0.04	1.8 ± 0.14
0.2 mol L^{-1} Na$_4$P$_2$O$_7$	2.3 ± 0.16	0.1 ± 0.01	1.8 ± 0.13
1 mol L^{-1} acetic acid	0.65 ± 0.05	0.15 ± 0.01	2.4 ± 0.2
0.5 mol L^{-1} acetic acid	0.6 ± 0.05	0.12 ± 0.01	1.6 ± 0.14
acetate buffer (pH = 5)	0.2 ± 0.02	0.02 ± 0.002	1.1 ± 0.1
1 mol L^{-1} CaCl$_2$	0.5 ± 0.04	0.05 ± 0.005	1.5 ± 0.12
1 mol L^{-1} NaCH$_3$COO	0.47 ± 0.04	0.04 ± 0.004	1.0 ± 0.1
1 mol L^{-1} NH$_4$CH$_3$COO	0.28 ± 0.02	0.02 ± 0.002	0.5 ± 0.06
1 mol L^{-1} KNO$_3$	0.24 ± 0.02	0.01 ± 0.001	1.4 ± 0.11

Table 3. Results of Pb, Cd and Ni contents in sewage sludge samples by using first sequential extraction (as mg kg^{-1} based on dried weight), $n = 3$

Extraction reagent	Fraction	Pb	Cd	Ni
1 mol L^{-1} KNO$_3$	exchangeable	0.2 ± 0.02	0.01 ± 0.001	1.1 ± 0.1
0.2 mol L^{-1} Na$_4$P$_2$O$_7$	Organic bound	2.2 ± 0.2	0.10 ± 0.01	1.5 ± 0.11
0.1 mol L^{-1} Na$_2$EDTA	Carbonate-amorph Fe oxide	8.8 ± 0.7	0.19 ± 0.014	2.0 ± 0.17
1 mol L^{-1} NH$_2$OH · HCl in acetic acid (25%)	adsorbed species on Fe–Mn oxides	3.5 ± 0.3	0.15 ± 0.012	1.5 ± 0.12
HNO$_3$/H$_2$O$_2$	residual	9.5 ± 0.8	0.6 ± 0.05	37 ± 3

Table 4. Results of Pb, Cd and Ni contents in sewage sludge samples by using second sequential extraction (as mg kg^{-1} based on dried weight), $n = 3$

Extraction reagent	Fraction	Pb	Cd	Ni
1 mol L^{-1} CaCl$_2$	exchangeable	0.5 ± 0.05	0.05 ± 0.005	1.5 ± 0.12
acetate buffer (pH = 5)	Carbonate	–	0.02 ± 0.002	1.0 ± 0.1
0.04 mol L^{-1} NH$_2$OH · HCl in acetic acid (25%)	Mn oxide occluded	2.2 ± 0.16	0.3 ± 0.026	1.7 ± 0.12
HNO$_3$/H$_2$O$_2$	residual	20 ± 1.5	0.72 ± 0.06	36 ± 3.1

Table 5. Results of Pb, Cd and Ni contents in sewage sludge samples by using third sequential extraction (as mg kg^{-1} based on dried weight), $n = 3$

Extraction reagent	Fraction	Pb	Cd	Ni
1 mol L^{-1} NaCH$_3$COO	exchangeable	0.47 ± 0.04	0.04 ± 0.004	1.0 ± 0.08
acetate buffer (pH = 5)	Carbonate	–	0.01 ± 0.001	0.5 ± 0.04
0.04 mol L^{-1} NH$_2$OH · HCl in acetic acid (25%)	Mn oxide occluded	2.4 ± 0.2	0.4 ± 0.04	1.4 ± 0.11
HNO$_3$/H$_2$O$_2$	residual	19 ± 1.4	0.5 ± 0.05	37 ± 3

cadmium concentrations of CaCl$_2$ and CH$_3$COONa extracts were higher than in the KNO$_3$ and NH$_4$CH$_3$COO extracts. These results can be explained by the formation of chloride and acetate complexes plus ion exchange. When NH$_4$CH$_3$COO was used, the pH was raised and this effect counters the metal complexation by acetate. Because acetic acid dissolves both the exchangeable species and may partly attack carbonate phases, the Pb and Cd levels in acetic acid extracts were higher than in the exchangeable
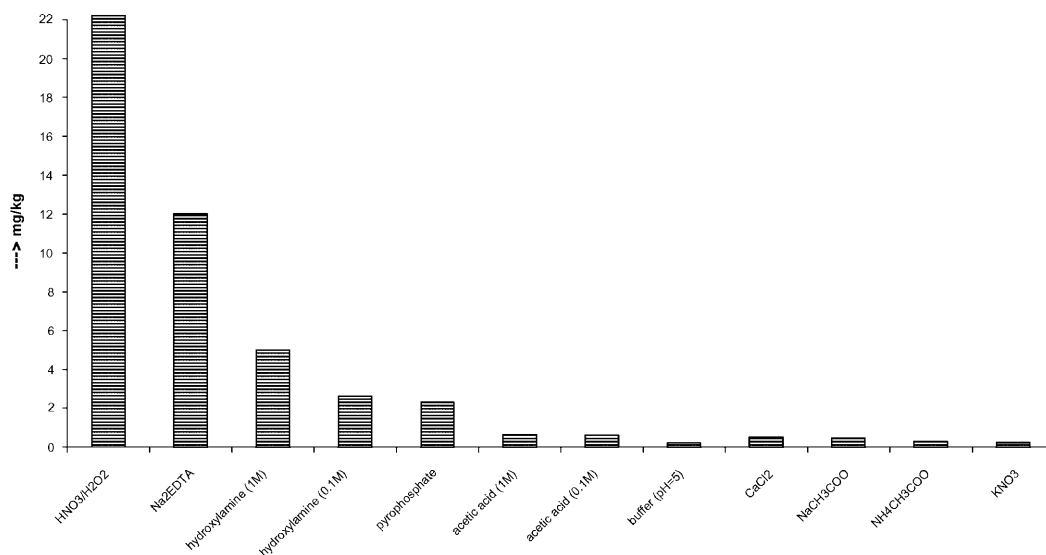
Fig. 1. Pb concentrations of different extracts in sewage sludge
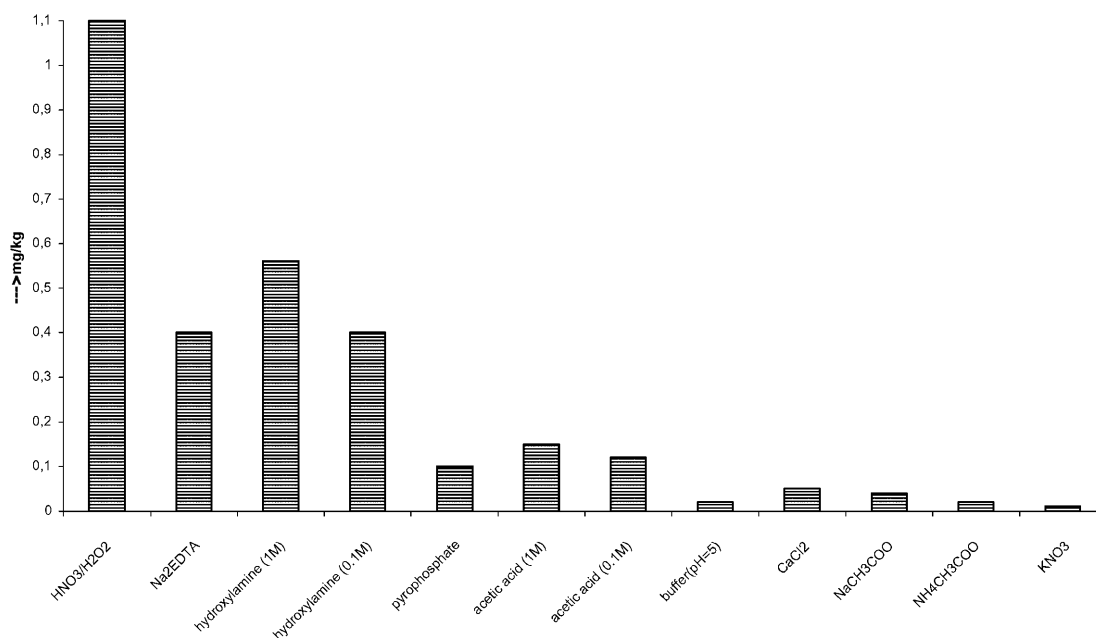
Fig. 2. Cd concentrations of different extracts in sewage sludge

extracts. In addition, higher Pb and Cd concentrations in both 0.5 and 1.0 mol L^{-1} acetic acid extracts were found than for the acetate buffer extracts. These results show that the acetate buffer (pH = 5.0) can not dissolve all carbonate phases of soil.

Organically bound metal species were generally determined by using $Na_4P_2O_7$ or EDTA as extractants. However, $Na_4P_2O_7$ was preferred to EDTA because EDTA will also dissolve the carbonate species.

According to the results in Table 2, while the $Na_4P_2O_7$ extract concentrations were found as 2.3 mg Pb L^{-1} and 0.1 mg Cd L^{-1}, the EDTA extract concentrations were found as 12.0 mg Pb L^{-1} and 0.4 1 mg Cd L^{-1}. On the other hand, the acetic acid extract and the acetate–acetic acid buffer (which dissolve the carbonate phase) extract concentrations were also found very low such as 0.65 and 0.2 mg L^{-1} for Pb and 0.15 and 0.02 mg L^{-1} for Cd, respectively. Therefore,

either $Na_4P_2O_7$ does not totally dissolve the organically bound Pb species or another explanation must be given for the very high Pb and Cd concentration of EDTA–soil extracts (for example, EDTA is extracting Pb and Cd in all sludge phases except from the silicate phase). The working group of Commission of European Community has also chosen EDTA to be regarded as extracting the metals in all the non-silicate-bound soil phases and is likely to reflect the metal availability in both the short-term and relatively long-term period [5]. Our results have also proven these conclusions.

It is described that the acidified $NH_2OH \cdot HCl$ solution releases the metals from the Mn and iron oxides (or hydroxide) at high concentrations of $NH_2OH \cdot HCl$ [5]. As it could be expected, an increase in the Pb and Cd concentration was found when the concentration of $NH_2OH \cdot HCl$ was increased from $0.04\,mol\,L^{-1}$ to $1.0\,mol\,L^{-1}$. From the Figs. 1 and 2, it is seen that the Pb concentration of EDTA extracts is higher than 50% of $HNO_3–H_2O_2$ extracts. Cd concentrations of $NH_2OH \cdot HCl$ extracts are higher than the EDTA–Cd-concentrations.
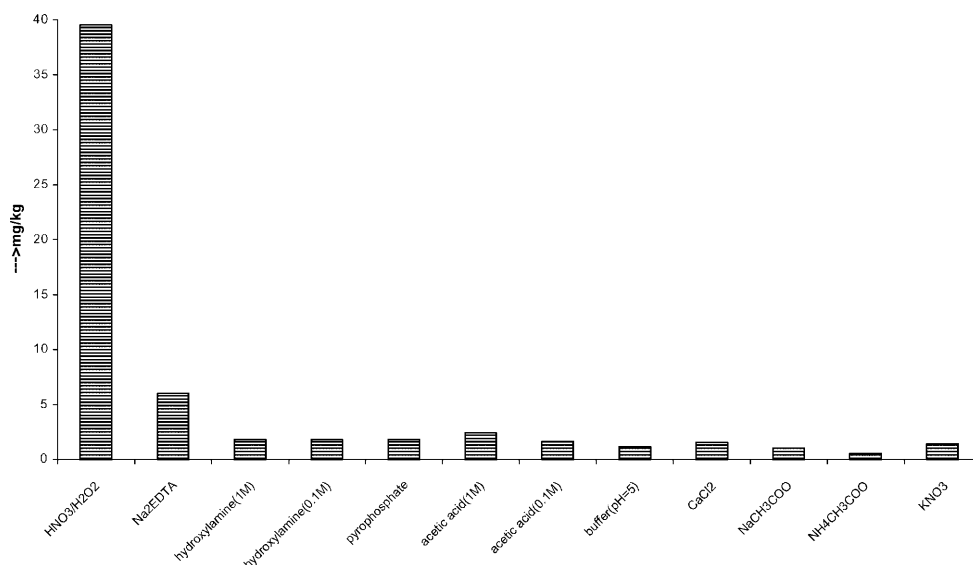
Total Pb and Cd contents of sewage sludge by using three sequential extractions were found to be very close to each other (Tables 3–5). The carbonate bound Pb species using acetic acid–acetate buffer (pH = 5) were found as zero. Because EDTA also attacks the other phases, Pb and Cd concentrations of this extract were found importantly high (Figs. 4–5).

The adsorbed lead species on oxide minerals (iron and manganese) by using $1\,mol\,L^{-1}$ $NH_2OH \cdot HCl$ were found around $3.5\,mg\,Pb\,L^{-1}$. Especially, identity of the results of first sequential extraction procedure comparing to the others is important because these extracts were containing adsorbed species on both Fe and Mn oxides. It should be noted that Pb and Cd concentrations and their percentage bound to the mobile phases are relatively high as 50%.
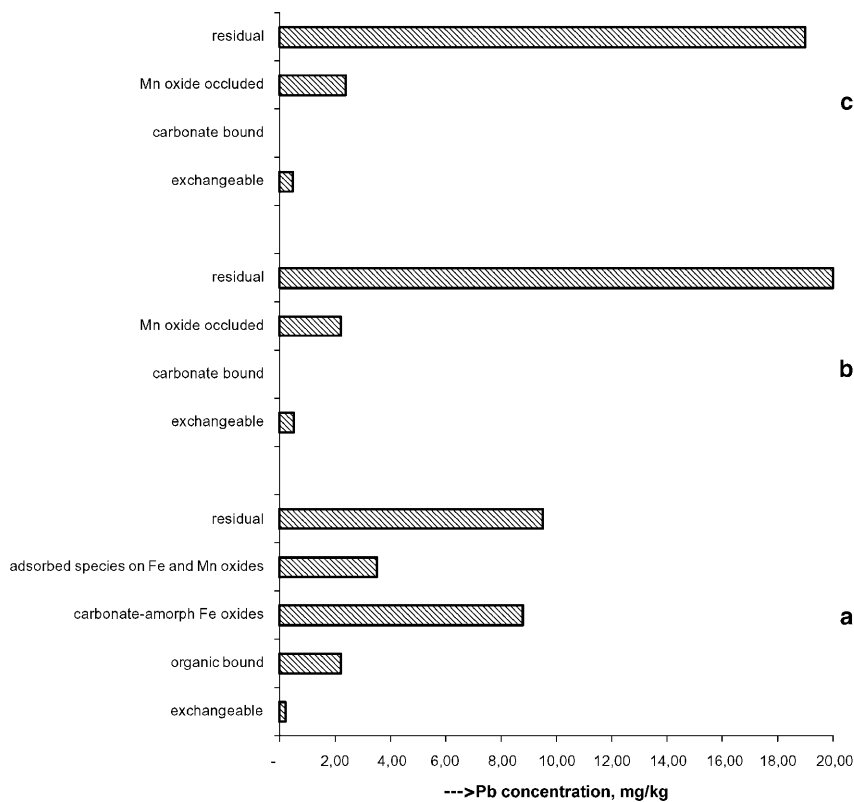
Nickel

On the contrary to Pb and Cd, the Ni concentrations from the examined selective extracts for exchangeable species were very close to each other because the formation of chloride and acetate complexes is not effective for Ni (the overall formation constant of $Ni–CH_3COO^-$ complex is 851). So, these extracts dissolve only the exchangeable species. Found Ni levels in acetic acid extracts were higher than the exchangeable extracts because the acetic acid dissolves both the exchangeable species and it may partly attack carbonate phases like Pb and Cd (Table 2). Ni concentrations of all applied selective and sequential extracts were relatively found low. This result was contributed to the fact that Ni species in sewage sludge are generally not mobile.
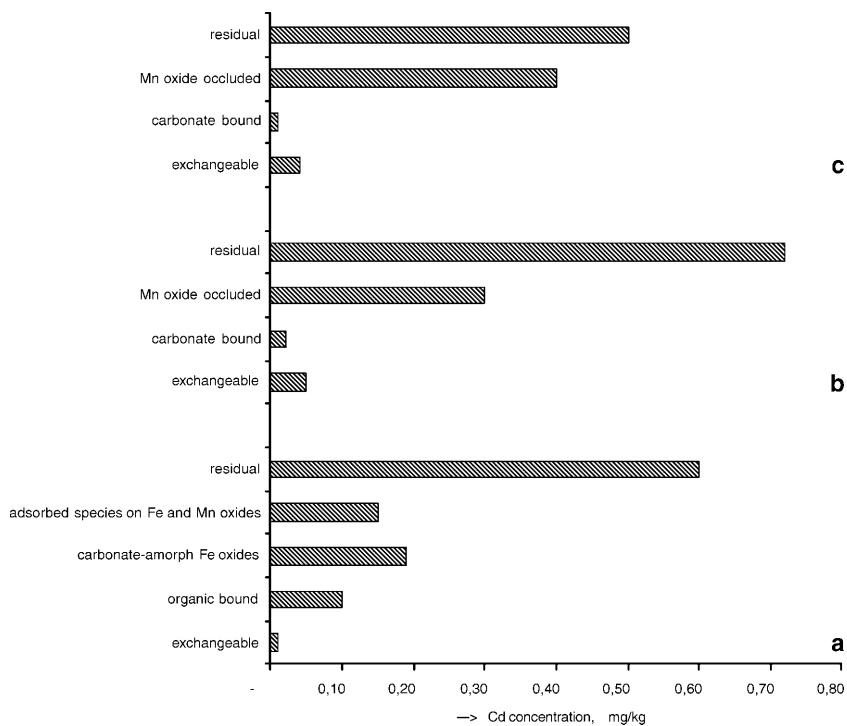
The adsorbed Ni concentrations on oxide minerals of iron and manganese were found to be around

**Fig. 3.** Ni concentrations of different extracts in sewage sludge

residual
Mn oxide occluded
carbonate bound
exchangeable

c

residual
Mn oxide occluded
carbonate bound
exchangeable

b

residual
adsorbed species on Fe and Mn oxides
carbonate-amorph Fe oxides
organic bound
exchangeable

a

-   2,00   4,00   6,00   8,00   10,00   12,00   14,00   16,00   18,00   20,00
--->Pb concentration, mg/kg

Fig. 4. Average amounts of different Pb forms in the sewage sludge by using various sequential extraction procedures. (a) from Miller and McFee, (b) modified from Tessier, (c) modified from Tessier

residual
Mn oxide occluded
carbonate bound
exchangeable

c

residual
Mn oxide occluded
carbonate bound
exchangeable

b

residual
adsorbed species on Fe and Mn oxides
carbonate-amorph Fe oxides
organic bound
exchangeable

a

-   0,10   0,20   0,30   0,40   0,50   0,60   0,70   0,80
—> Cd concentration, mg/kg

Fig. 5. Average amounts of different Cd forms in the sewage sludge by using various sequential extraction procedures. (a) from Miller and McFee, (b) modified from Tessier, (c) modified from Tessier

$1.6\,mg\,L^{-1}$ (Tables 2–5). When acetic acid concentration increase from $0.5\,mol\,L^{-1}$ to $1.0\,mol\,L^{-1}$ (from Table 2), Ni level of soil extract increases about 50%. Ni concentrations of different sequential extracts in sewage sludge were given as scheme in Fig. 3.
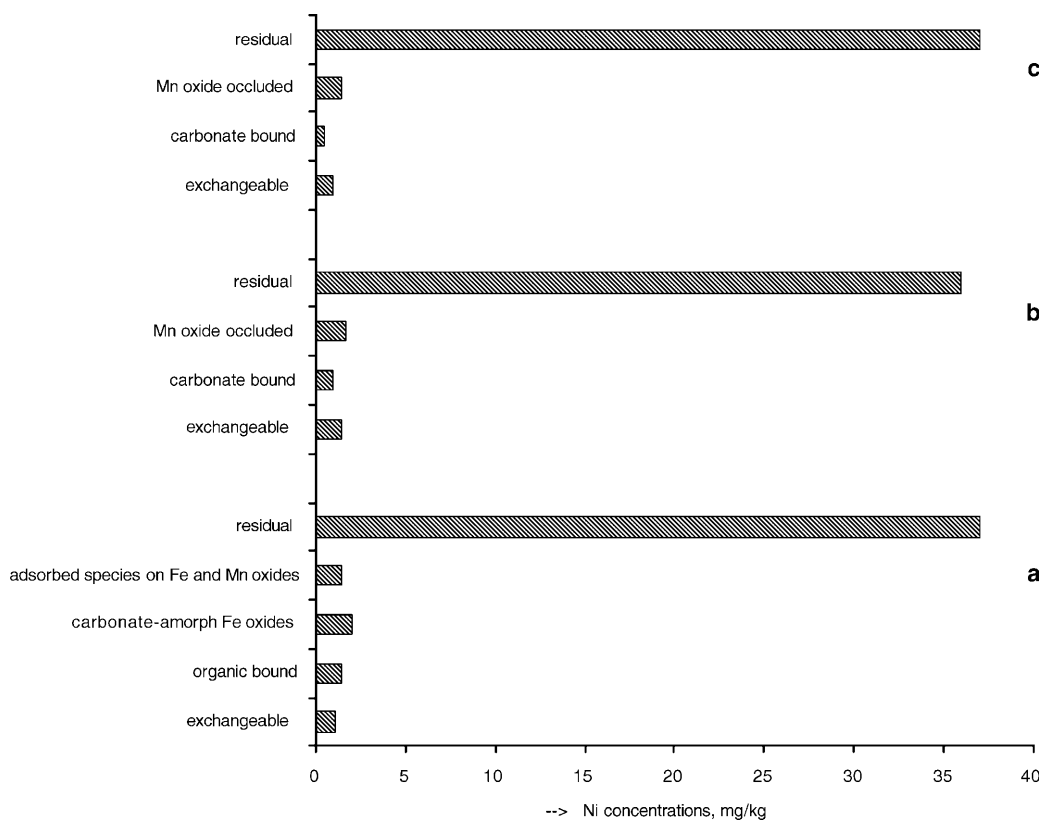
Fig. 6. Average amounts of different Ni forms in the sewage sludge by using various sequential extraction procedures. (a) from Miller and McFee, (b) modified from Tessier, (c) modified from Tessier

Conclusions

Different selective chemical reagents and the modified three sequential extraction procedures used in this work were found useful to determine the mobility and chemical forms of Pb, Cd and Ni in sewage sludge. The results obtained show that 50% of Pb, 36% of Cd and 15% of Ni in the sewage sludge studied are in the mobil form in Na_2EDTA extracts.

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