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HEAVY METAL MOBILITY IN SOILS UNDER THE APPLICATION OF SEWAGE SLUDGE

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Abstract

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One of the main issues relating to sewage sludge (SS) disposal is the introduction of heavy metals and organic pollutants. The aim of this research work was to assess the mobility of heavy metals via measurement of the soluble and easily exchangeable metals in soils on which sewage sludge had been deposited 10 years before analysis and clarify patterns and relationships between heavy metals in the amended soils as opposed to un-amended control soils. There are few studies on the leaching potential of heavy metals in sludge-amended soils through measurement of the soluble and easily exchangeable metal forms. Mobile heavy metals (soluble + easily exchangeable Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) were measured via extraction with 0.05 M $Ca(NO_3)_2$. We observed: (i) elevated Cd, Cr, Zn and Cu concentrations in the sludge treated soils; (ii) no effect of sludge application was found, as far as Pb, Mn, Fe, Ni and Co mobilities are concerned; (iii) the statistical analysis showed that slight perturbations in heavy metals relationships were observed in the sewage sludge treated soils in comparison with the control soils, especially as Cu and Cr sources of soluble forms are concerned; (iv) concentrations of the nine measured elements fall in the background range of published data on wide variety of soils.

Key words: soil, sewage sludge, heavy metals

Introduction

Heavy metal transfer in soil profiles is a major environmental concern because even slow transport through the soil may cause deterioration of groundwater quality. The use of sewage sludge from wastewater treatment plants for amendment of agricultural lands is on the rise in the past 10 years. One of the main issues relating to sewage sludge amendments is the introduction of heavy metals and organic pollutants into the soil. There have been numerous reports on land waste disposal, which deal with the chemical aspects of fertility and pollution (Williams et al., 1987; Alloway and Jackson, 1991; Giusquiani et al., 1992; Kasatikov and Runik, 1994; Bacon et al., 2001; Jakubus and Czekała, 2001). The concentration of a given heavy metal in soil varies with depth depending on the metal species and soil properties. Because of strong binding to the different soil components, heavy metals from external sources accumulate in the upper layers and their concentration decreases very rapidly with depth. Sauerbeck (1991) reported that metal quantities observed in deeper layers of the soil are not specific of an element. It is therefore assumed that transport occurs through binding to small soil particles that are carried in the soil profile. Extensive research conducted over the past 20 years on metal movement in sludge-amended soils has shown that metals mobility in soils is very low even under conditions, which raise their mobility. The transport mechanisms of heavy metals through the soil pro-

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file has long presented great interest to the scientific community because of the possibility of groundwater contamination through metal leaching Kanungo and Mohapatra (2000).

There are few studies, however on the leaching potential of heavy metals in sludge-amended soils through measurement of the soluble and easily exchangeable metal forms. The aim of this research work was to assess the mobility of heavy metals in soils on which sewage sludge had been deposited 10 years before analysis and clarify patterns and relationships between heavy metals in the amended soils as opposed to un-amended control soils. This study is a continuation of our previous research (Atanassova et al., 2005; Atanassova et al., 2006) concerning the physico-chemical and eco-chemical status of former sewage sludge treated soils near the Sofia Waste Waste Treatment Plant (WWTP).

Materials and Methods

I. Study sites and soils

The study was based on adjacent plots amended with sewage sludge (SS), 40 and 60 t/ha (Marinova, 2002) near the Sofia Waste Water Treatment Plant (WWTP). This trial was brought to an end in 1994, and sampling took place in 2003, that is nearly 10 years following sludge application. In our study, we sampled plots treated with 40 t/ha and 60 t/ha SS-treated soils and control soil profiles. Data on soil physico-chemical properties and organic carbon contents are presented in Atanassova et al. (2005). In brief, the main physico-chemical parameters influencing heavy metal mobility, i.e. pH , total organic carbon and CEC and of the soil profile horizons vary from: pH 6.3 – 7.0 (40 t/ha SS treated soil), total organic carbon TOC 1.4 – 0.8 %, CEC 34.2 – 42 $cmol_+$/kg; and pH 7.3 – 7.9 (60 t/ha SS treated soil), TOC: 1.1 – 0.2 %, CEC 34.7 – 39.2 $cmol_+$/kg; control soil characteristics: pH 6.5 – 7.2; TOC 1.4 – 0.4%; CEC from 34.5 – 29 $cmol_+$/kg in the lowest depth. The heavy metal contents fall into the range of the maximum permissible levels imposed by the EU (Tsadilas et al., 2000) and the values for most of the measured heavy metals fall below the maximum acceptable concentrations in sludge given by Webber et al. (1984), IEEP, 2009 and the Bulgarian standards (Sludge Directive, State Gazette No 112, 2004).

II. Methods of soil analysis

***Extraction*: **Mobile heavy metals, soluble + easily exchangeable (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) were measured via extraction with 0.05 M Ca $(NO_3)_2$ in a ratio 1:10 (McGrath and Cegarra, 1992; Gray et al., 1999; Mule and Melis, 2000; Atanassova et al., 2005) and determined by ICP- AES. The use of the dilute salt of Ca renders mobile the soluble metals and the weakly exchangeable forms and is indicative of the active mobile and bioavailable pool. This weak extractant gives an estimation of the desorption potential of these metals and more or less mimics the normal ionic strength of soil solutions (0.01 M Ca^{2+}) as used in desorption experiments (McLaren et al., 1990; Atanassova and Okazaki, 1997; Atanassova, 1999).

Analytical specifications

Instrumentation

The analytical inductively coupled plasma atomic emission spectrometry (ICP-AES) experiments were performed with a Jobin Yvon (Longjumeau, France) radial viewing 40,68 MHz "ULTIMA 2" ICP-AES equipment and ICP operating conditions as follows:

Incident power - 1.05 kW; outer argon flow rate - 12.0 l min-1 ; liquid uptake rate - 1.0 ml min-1 ; auxiliary gas - 0 l min-1 ; sheath gas flow rate - 0.2 l min-1; carrier gas flow rate - 0.8 l min-1; nebulizer pressure flow - 2.8 bar; Mg II 280.270 nm / Mg I 285.213 nm line intensity ratio - 11.0. The quantitative information about the type of spectral interferences was derived from wavelength scans for 100 pm wide spectral window around the candidate (prominent) analysis lines of Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn in the presence of Al, Ca, Mg, Fe, Ti, Mn, Na, P and K as interfering elements separately.

Reagents, test solutions and certified reference materials

Reagents of highest purity grade were used: 30 % HCl and 65 % HNO_3 (Suprapur, Merck) and deionized water. Stock solutions of the analyte (1 mg ml^{-1}) and standard solutions were prepared from Merck ICP-AES mono and multi - element standard solutions. Standard reference material of natural water TMDA 51-2 was used to improve the accuracy of the analytical results.

ICP AES analysis

Before the ICP AES analysis the samples were acidified and filtered through 0,45 μm membrane filter, according to the requirements of ISO 5667 "Water quality – Sampling" - 2009. Nine chemical elements (Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn) were analized referred to ISO 22036: 2008: Soil quality "Determination of trace elements in extracts of soil by inductively coupled plasma - atomic emission spectrometry (ICP - AES)" and ISO 11885:2007, Water quality "Determination of selected elements by inductively coupled plasma optical emission spectrometry (ICP-OES)". To improve the accuracy of the analytical results the investigated elements were determined with their both prominent lines, free from spectral interferences coming from the matrix components (Al, Ca, Mg, Fe, Ti, Mn, Na, P and K). Standard reference material of natural water TMDA 51-2 was applied for evaluation of the accuracy and repeatability of the obtained analytical results, for each group of samples.

III. Statistical Analysis

Multivariate statistical analysis was employed using SPSS 19 for Windows in order to identify distribution patterns and perturbations in heavy metals relationships in the sewage sludge (SS) treated and control soil profiles. Principal component analysis (PCA) was conducted and the factors with an eigenvalue > 1 were extracted. Differences between heavy metal soluble concentrations were analysed using the t-test ($P \leq 0.05$).

Results and Discussion

Heavy metal mobility

In general, only Cd and Cr showed higher statistically significant differences in concentrations of soluble forms throughout the soil profiles of the 60 t/ha SS treated soil, as compared with the 40 t/ha and the control soil (Figure 1a,b,c). Cadmium concentrations were similar to those analyzed by GF AAS (Graphite Furnace) reported by Atanassova et al. (2005) in the same soil profile. We also observed higher soluble + weakly exchangeable Co concentrations in the 40 t/ha and 60

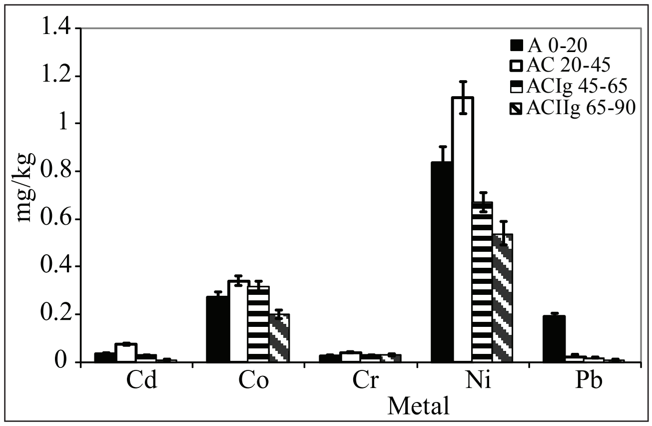

Fig. 1a. Mobile forms of heavy metals in the 40 t/ha SS treated soil

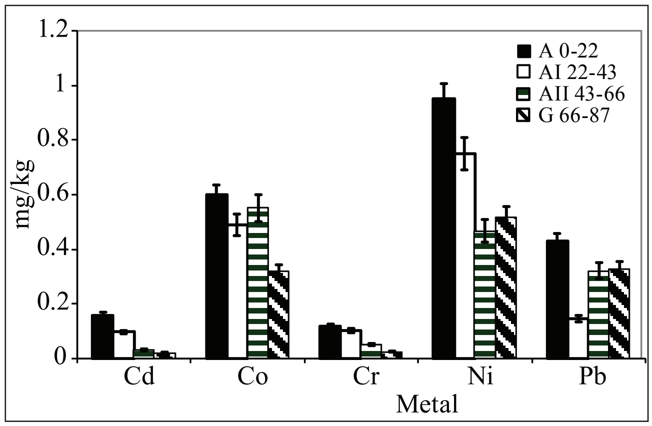

Fig. 1b. Mobile forms of heavy metals in the 60 t/ha SS treated soil

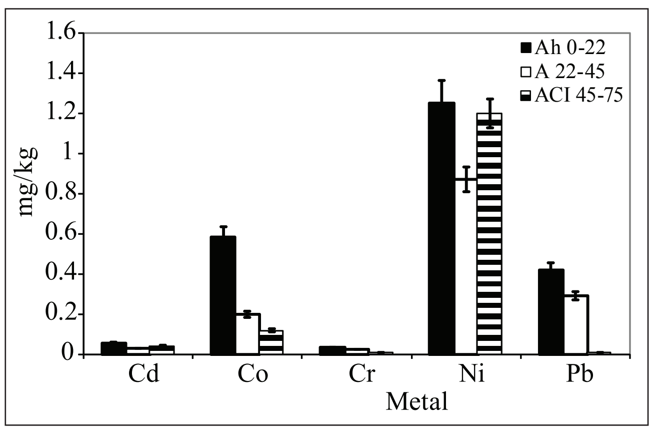

Fig. 1c. Mobile forms of heavy metals in the control soil

t/ha treated soil (Figure 1a, b) though the control soil exhibits similar concentrations in the upper horizon, therefore we cannot attribute this to the effect of the sludge, but to natural pedogenic sources. Nickel shows similar concentrations in the two soil profiles and the control soil and tendency to maintain nearly equal solubilities downwards the soil profiles. Cd solubility was higher in the 60 t/ha SS treated soil than in the 40 t/ha SS treated soil and the control variant (Figure 1a, b, c). These values fall in the range of the natural background mobile concentrations reported by McGrath and Cegarra (1992) and Hornburg et al. (1995) who used 0.1 M $Ca(NO_3)_2$ and 0.1 $MCaCl_2$. No accumulation of Pb due to sewage sludge treatment was detected in the treated soils, (Figure 1a, b, c), however elevated concentrations were observed in the deeper G horizons of the 60 t/ha SS treated soil affected by gleyification. This is due to the higher pH of the 60 t/ha SS treated soil reaching pH 7.9 (Atanassova et al., 2005) in the sub-surface horizon. These elevated mobile Pb concentrations are attributed to formation of soluble organic complexes at near neutral and slightly alkaline pH (Brümmer and Herms, 1983; Marschner et al., 1995). These concentrations are higher than those reported in Atanassova et al. (2005) achieved by GF AAS measurement owing to the analytical specifications and differences in the spectral characteristics of Pb using ICP AES and AAS GF. In the upper layer of the control soil, the accumulation of soluble Pb could be due to atmospheric deposition and closeness to the motorway of the site. Effect from sludge application is, however not evident, as no elevated concentrations in the upper soil layers of the SS treated soils were observed.

Mn and Fe did not differ statistically between the control soil profile and the amended soils and most probably, their soluble concentrations reflect natural pedogenic processes, without a clear effect from the sludge application (Figure 2 a, b, c, Figure 3). In general, higher Mn concentrations in all the soils analysed were observed in this study as compared with median values in arable and grassland soils in Germany, which could be due to biogenic sources of Mn (Hornburg et al., 1995).

Higher soluble Zn was detected, especially in the upper surface and sub-surface horizons of the SS treated soils (highest in the 60 t/ha variant, Figure 2 a, b, c) than in the control soil, because of the sludge applica-

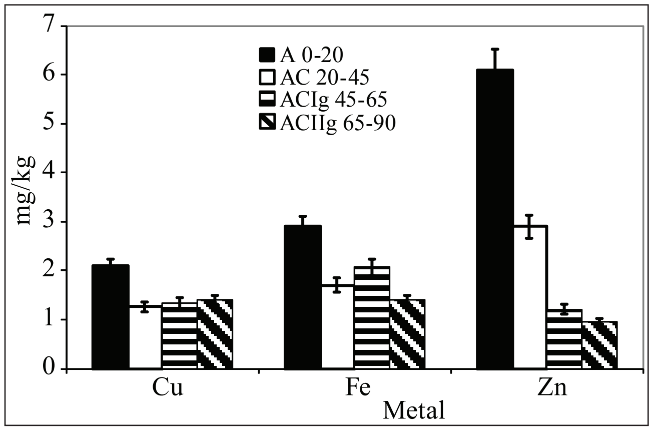

Fig. 2a. Mobile forms of heavy metals in the 40 t/ha sewage sludge treated soil

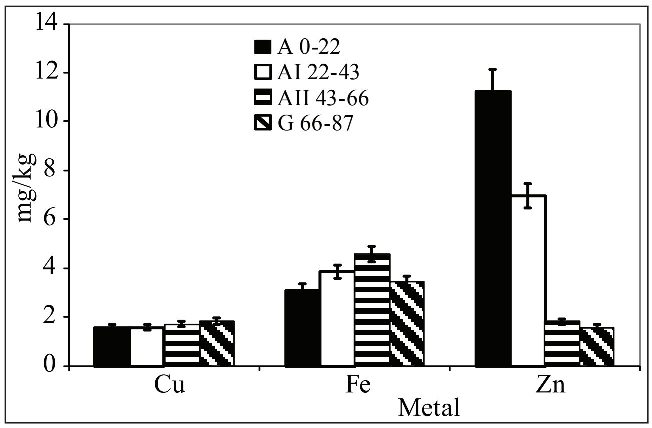

Fig. 2b. Mobile forms of heavy metals in the 60 t/ha sewage sludge treated soil

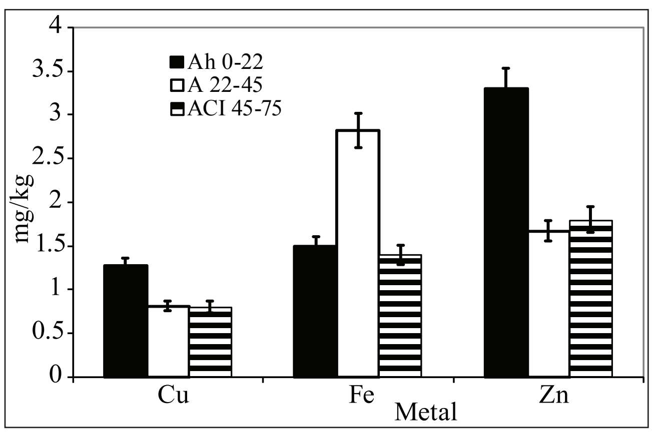

Fig. 2c. Mobile forms of heavy metals in the control soil

tion. Higher significantly different Cu concentrations were detected in the upper surface layers and throughout the profile depths, i.e. translocation and accumulation of mobile Cu in the deeper layers of the SS treated soils due to the sludge source and the soil characteristics, (Figure 2 a, b, c). This behavior could be attributed to the similar chemistry of the Cu complexes at near neutral and slightly alkaline pH with the Pb complexes, therefore similar trends in Cu and Pb distribution are often observed. Copper and zinc soluble concentrations of amended and control soils fall in the higher range of detected concentrations in arable, grassland and forest soils as reported in Hornburg and Brummer (1993) and Hornburg et. al. (1995).

Statistical analysis

We carried out principal component analysis to examine the interrelations among the mobile heavy metals (variables) in order to identify the underlying structure of these variables.

As higher concentrations of some heavy metals were encountered in the 60 t/ha SS treated soil, we carried out principal component analysis on the 60 t/ha SS-amended soil and separately on the control soil in order to differentiate between factors extracted and patterns in metals relationships. The correlation matrix of the 60 t/ha SS treated soils (Table 1) shows that only Cr and Cu are weakly or not correlated to the other heavy metals. Three principal components (PC) were identified with eigenvalues > 1, explaining 53%, 23.7% and 12.6% of the total variance (89.4%) (Table 2). The eigenvalue is a numeric estimation of how much of the variation each component explains. In the control soil, however two principal components were identified with eigenvalues > 1 explaining 81.3% and 18.7% of the total variance (100%) (Table 4). Significant and close correlations (Table 3) were observed between nearly all the heavy metals in the control soil showing similar source and/or behavior. In the sewage sludge treated soil the first PC (Table 2) was loaded by nearly all heavy metals excluding Cr, Cu. Cr loaded the second PC, and the third slightly by Cu. Chromium was also loading the third principal component. In the control soil, different pattern loadings were obtained. All the heavy metals loaded PC1 with slight loadings of PC2 by Pb, Fe and Cr (Table 4).

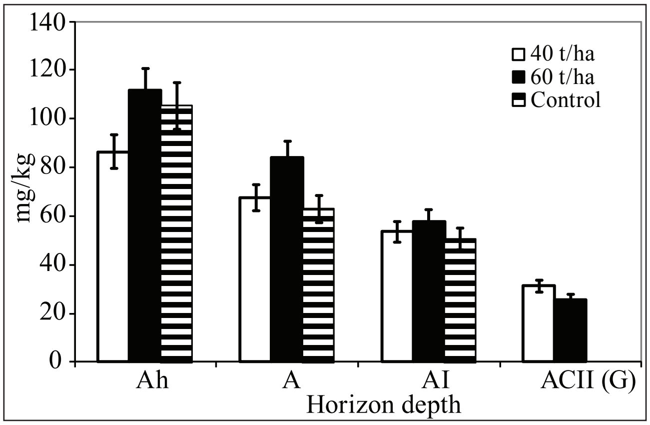

Fig. 3. Mobile Mn in the soil profile of the sewage sludge treated and control soils

Table 1
Correlation matrix of soluble heavy metals in the 60 t/ha treated soil

		Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Correlation	Cd	1.000	.699	.000	-.247	.549	.679	.951	.282	.247
	Co	.699	1.000	-.074	-.579	.608	.776	.709	.641	.311
	Cr	.000	-.074	1.000	-.461	-.752	-.232	.103	-.547	.006
	Cu	-.247	-.579	-.461	1.000	.121	-.041	-.298	.025	.284
	Fe	.549	.608	-.752	.121	1.000	.771	.538	.783	.354
	Mn	.679	.776	-.232	-.041	.771	1.000	.767	.803	.770
	Ni	.951	.709	.103	-.298	.538	.767	1.000	.338	.408
	Pb	.282	.641	-.547	.025	.783	.803	.338	1.000	.650
	Zn	.247	.311	.006	.284	.354	.770	.408	.650	1.000

Table 2
Component matrix for the 60 t/ha SS treated soil

	Component		
	1	2	3
Cd	.769	.404	-.067
Co	.846	.362	-.224
Cr	-.322	.796	.505
Cu	-.136	-.813	.352
Fe	.847	-.387	-.323
Mn	.969	-.043	.215
Ni	.811	.438	.092
Pb	.807	-.393	-.010
Zn	.613	-.228	.736

Table 4
Component matrix for the control soil

	Component	
	1	2
Cd	.772	-.635
Co	.968	-.249
Cr	.889	.459
Cu	.979	.203
Fe	.806	.592
Mn	.876	-.482
Ni	.999	-.046
Pb	.858	.513
Zn	.939	-.344

Table 3
Correlation matrix of soluble heavy metals in the control soil

		Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
Correlation	Cd	1.000	.906	.395	.627	.246	.983	.801	.337	.944
	Co	.906	1.000	.746	.898	.633	.969	.979	.703	.995
	Cr	.395	.746	1.000	.963	.988	.557	.867	.998	.676
	Cu	.627	.898	.963	1.000	.909	.760	.969	.945	.849
	Fe	.246	.633	.988	.909	1.000	.421	.778	.996	.553
	Mn	.983	.969	.557	.760	.421	1.000	.897	.504	.989
	Ni	.801	.979	.867	.969	.778	.897	1.000	.834	.954
	Pb	.337	.703	.998	.945	.996	.504	.834	1.000	.629
	Zn	.944	.995	.676	.849	.553	.989	.954	.629	1.000

The statistical analysis and the depth distribution of the soluble heavy metals in the treated and control soils reveals that the chemistry of the nine heavy metals is governed mainly by pedogenic sources in the lower depths and anthropogenic sources in the surface horizons with the exception of Cu and Cr whose sources of solubility are different from the other metals..

Conclusions

We analyzed the soluble and readily exchangeable pool of nine heavy metals in sewage sludge treated soils with the purpose to assess metals leaching and determine the effect of the sludge application. To further assess the structure in the data obtained and the relationships between the elements we carried out statistical analysis.

These are our key findings:

- elevated Cd, Cr, Zn and Cu concentrations were observed in the sludge treated soils.
- no effect of sludge was found as far as Pb, Mn, Fe, Ni and Co are concerned.
- the statistical analysis showed that slight perturbations in heavy metals relationships were observed in the SS treated soils in comparison with the control soils as far as Cu and Cr sources of soluble forms are concerned, therefore their mobility was different in the sludge treated soil.
- although the effect of sludge application on the soils studied is obvious, still concentrations of the nine measured elements fall in the range of background levels as compared with published data on wide variety of soils.

References

Alloway, B. J and A. P. Jackson, 1991. The behaviour of heavy metals in sewage sludge-amended soils. *The Science of The Total Environment*, **100**: 151-176.

Atanassova, I. and M. Okazaki, 1997. Adsorption - desorption characteristics of high levels of copper in soil clay fractions. *Water, Air and Soil Pollution*, **98**: 213-228.

Atanassova, I., 1999. Competitive effect of Copper, Zinc, Cadmium and Nickel on ion adsorption and desorption by soil clays. *Water, Air and Soil Pollution,* **111**: 115-125.

Atanassova, I., S. Marinova, M. Teoharov and E. Filcheva, 2005. Present status of past sewage sludge treated soils. Impacts on Cd and Pb mobility. In Proc."Management, Use and Protection of Soil Resources" National Conf. with Inter. Particip. 15-19 May Sofia, pp. 409-414.

Atanassova, I., M. Teoharov, S. Marinova and E. Filcheva, 2006. Sewage sludge storage on soils around a waste-water treatment plant. Impact on some soil properties. *Bulgarian Journal of Agricultural Science,* **12**: 51-62.

Bacon, J. R., C. D. Campbell, M. C. Coull, B. J. Chambers, P. A. Gibbs, A. Chaudri, S. P. McGrath, **Carlton-Smith and C. Aitken,** 2001. A long-term study on the effects of heavy metals in sewage sludge on soil fertility and soil microbial activity. In: Recycling and reuse of sewage skudge. Dhir, R. K., et al., eds., Thomas Telford, London (Publ), pp. 87-96.

Brümmer, G. and U. Herms, 1983. Influence of soil reaction and organic matter on the solubility of heavy metals in soils, In: B. Ulrich and J. Pankrath (eds.) Effects of Air Pollutants in Forest Ecosystems. D. Reidel Dordrecht, pp. 233-243.

Giusquiani, P.L., Gigliotti, G. and D. Businelli, 1992. Mobility of heavy metals in urban waste-amended soils. *Journal of Environmental Quality*, **21**: 330 – 335.

Gray, R. G. McLaren, A. H. C. Roberts and L. M. Condron, 1999. Cadmium phytoavailability in some New Zealand soils. *Australian Journal of Soil Research*, **37**: 461 – 478.

Hornburg, V. and G. W. Brummer, 1993. Behaviour of heavy metals in soils. 1. Heavy metal mobility. *Zeitschrift fur Pflanzenernahrung und Bodenkunde*, **156:** 467–477.

Hornburg, V., G. Welp and G. W. Brümmer, 1995. Verhalten von Schwermetallen in Boden. 2. Extraction mobiler Schwermetalle mittels $CaCl_2$ und NH_4NO_3. *Z. Pflanzenernahr. Bodenk.*, **158:** 137-145.

IEEP, 2009. Report on the Implementation of the Sewage Sludge Directive 86/278/EEC. http://ec.europa.eu/environment/waste/reporting/pdf/Sewage%20sludge_Directive.pdf.

Jakubus, M. and J. Czekała, 2001. Heavy Metal Speciation in Sewage Sludge. *Polish Journal of Environmental Studies,* **10**: 245-250.

Kanungo, S. B. and R. Mohapatra, 2000. Leaching Behavior of Various Trace Metals in Aqueous Medium from Two Fly Ash Samples. *Journal of Environmental Quality*, **29**: 188-196.

Kasatikov, B. and V. Runik, 1994. Approach to behavior of microelements in the soil-plant system in case of WWTP sewage sludge amendments. *Agrochemistry,* (No 5): 53 – 55 (Ru).

Marinova, S., 2002. Agroecological Assessment of sludges from Waste Water Treatment Plants and Major Approaches in Agriculture Utilization. Habilitation Thesis, Sofia, National Centre of Agrarian Sciences (Bg).

Marschner, B., U. Henke and G. Wessolek, 1995. Effects of meliorative additives on the adsorption and binding forms of heavy metals in contaminated topsoil from a former sewage farm. *Z. Pflanzenernahr. Bodenk.*, **158**: 9-14.

McGrath, S. P. and J. Cegarra, 1992. Chemical extractability of heavy metals during and after long-term applications of sewage sludge to soil. *Journal of Soil Science,* **43**: 313-21.

McLaren, R. G., D. S. Hogg and R. S. Swift, 1990. Some factors affecting the availability of native and applied soil copper in New Zealand soils. *Forest Ecology and Management*, **37**: 131-142.

Mulè, P. and P. Melis, 2000. Methods for remediation of metal – contaminated soils: preliminary results. *Communications in Soil Science and Plant Analyses*, **31**: 19&20, 3193-3204.

Sauerbeck, D. R., 1991. Plant element and soil properties governing uptake and availability of heavy metals derived from sewage sludge. *Water, Air, & Soil Pollution*, **57-58**: 227-237, doi: 10.1007/BF00282886

Sludge Directive, State Gazette, No 112, 2004.

Tsadilas, C., S. Rousseva, E. Filcheva, P. Bojinova, V. Samaras, K. Chakalov, G. Petkova, l. Stanislavova, I. Hristov, S. Marinova, V. Valev, V. Krasteva, T. Popova and H. Setatou, 2000. Greek-Bulgarian Research Project in Agroecology: Agricultural Use of Sewage Sludge and its impact on Physical and Chemical properties of Soil. *Journal of Balkan Ecology*, **3** (No2): 9-47.

Webber, M. D., A. Kloke and J. C. Tjell, 1984. In: Processing and Use of Sewage Sludges, eds. L"Hermite, P. and Ott, H.D. Riedel, Dordrecht (1984), pp. 371-386.

Williams, D. E., J. Vlamis, A. H. Pukite and J. E. Corey, 1987. Metal Movement in sludge-amended soils: A nine-year study. *Soil Science*, **143**: 124-131.

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