APPLICATION OF SEWAGE SLUDGE AND INFLUENCE ON SOIL PROPERTIES AND HEAVY METAL AVAILABILITY. A CASE STUDY IN THE THESSALONIKI PLAIN – GREECE.

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ABSTRACT

The amended soils chemical properties as affected by the application of a single dose of sewage sludge were evaluated over a one-year period. Three soil groups depending on pH values were examined. Data on pH, organic matter, $CaCO_3$, electrical conductivity, exchangeable Ca and Mg and concentration of nine metals (Cd, Co, Cr, Pb, Zn, Ni, Fe, Mn, Cu) before the application of sewage sludge in 2013 and after the wheat growing period in 2014, were statistically analyzed. Results showed that the lime stabilized sewage sludge significantly increased the electrical conductivity, $CaCO_3$ and Mg in all soil groups as well as pH and Ca of acidic soils, while the organic matter was not affected. The DTPA-extractable concentrations of most metals were significantly decreased. Zinc was the only metal that increased compared to the initial soil status. It is concluded that the application of lime stabilized sewage sludge to soils may be applied with no risk of increasing heavy metal bioavailability to phytotoxic levels. Further benefits to crops are provided by favoring pH conditions for plant growth in acidic soils and by improving plant nutrition via nitrogen addition. Moreover, the procedure can be an effective way of disposal of these residues.

Keywords: sewage sludge application, soil amendment, heavy metals, lime stabilization

1. Introduction

Since 2006, more than 80% of the national population equivalent wastewater load in Greece has been treated according to national and European legislation demands in order to protect the environment from the adverse effects of the wastewater discharges (Mathioudakis *et al*., 2013). Sewage sludge (SS) is one of the final products of the treatment of sewage at wastewater treatment plants. Co-disposal of this sludge at solid waste sanitary landfills is not a viable long-term alternative and the clear tendency within the EU is to minimize the disposal of biodegradable wastes to sanitary landfills, promoting in this way the options of recycling, composting, energy production and recovery. In the case of municipal SS, a major reuse method is the agricultural utilization of sludge as a soil amendment and/or fertilizer (Andreadakis *et al*., 2001). SS usually contains high levels (10% to >20%) of organic matter and is rich in N and P that are essential for plant growth (Antoniadis, 2008). Its application in forest, agronomic and silvopastoral systems as a fertilizer or a soil amendment, resulting in improved soil fertility, has been evaluated in many studies (Mosquera-Losada *et al*., 2001; Cuevas *et al*., 2003; Suchkova *et al*., 2010). On the other hand, SS constitutes a serious environmental problem requiring a safe and economical disposal. Europe, USA, and Asian countries already use SS in agriculture by taking advantage of its useful characteristics for soils and plants. SS disposal in Greece remains a serious problem since 30 years after the adoption of the rules for the agricultural use of SS from the EU under the Directive 86/278/EC (CEC, 1986), in essence its use in agriculture is very limited. Therefore, the management of SS is of significant importance for Greece. However, a proper attention should be paid on the impacts of its use on soil health, crop quality and heavy metal toxicity and leaching (Tsadilas *et al*., 2014). In this study, SS from the waste water treatment plant (WWTP) of Thessaloniki – Greece was applied in the fields in 2013. In order to assess the effects of sewage sludge application on the soils chemical properties and heavy metal availability, the soil chemical properties of 203 fields before and after a year period of the application, were investigated.

2. Materials and methods

The WWTP of Thessaloniki city serves about 1 million residents by treating daily 170.000-180.000 m^3 of raw wastewater. The treatment process includes screening, grid removal, primary sedimentation without the use of chemical coagulants, conventional activated sludge treatment with simultaneous denitrification, final sedimentation and effluent disinfection using chlorine gas (Cl_2). SS is anaerobically digested, thickened, and dewatered, giving a final product of about 20-22% in solids (Suchkova *et al*., 2010). SS is stored to a specially designated part of the plant. Stored sludge is stabilized with the addition of sufficient quantities of lime in order to raise the pH to 12. Until 2010 there was no provision for the reuse of the lime-treated stored sludge. In the following years reuse grew annually providing an alternative soil enhancement product for crops.

SS from the WWTP of Thessaloniki Greece was applied as a single dose during November – December 2013 in randomly chosen fields from the Thessaloniki Plain. Applied quantities ranged between 2 and 18 $Mgha^{-1}$ with the majority being above 9 $Mgha^{-1}$ and an average of 10 $Mgha^{-1}$ (on dry weight basis). SS was incorporated into the topsoil with a plowing depth of 15 cm. The main cultivated crop was winter wheat. Soil samplings were conducted from a depth of 0–30 cm during summer 2013, before the sewage sludge application, and summer 2014, one year after the application.

The required amount of SS was estimated based on the essential nutrients (N, P, K), pH and $CaCO_3$. EU Directive 86/278/EC, regarding heavy metal concentrations, was also considered. Following the usual agricultural practice in the area, conventional fertilizer was also applied in smaller quantities, to meet crop nutrient requirements. To facilitate SS amount estimation for soil application, a user friendly software was developed by the Soil Science Institute (SSI) of Thessaloniki - ELGO DIMITRA. The software also estimates the required fertilization doses, after SS application, depending on the cultivated crop.

SS and soil analyses were performed in the SSI of Thessaloniki. The samples were air-dried, ground, passed through a 2 mm sieve and analyzed, in four replications for selected chemical properties. Electrical conductivity (EC) was measured in the saturation extract and pH in the SS saturation paste, organic matter was determined gravimetrically by the mass loss at 240^oC, $CaCO_3$ was estimated using acid neutralization, NO_3-N was determined spectrophotometrically, NH_4-N by the salicylate method and measured using spectrophotometer, total N by the Kjeldahl method, K by the ammonium acetate method at pH 7, available P by the sodium bicarbonate method, available metals by the DTPA method and measured in ICP-OES, and total heavy metals were determined through an *Aqua Regia* extraction procedure (MEWAM, 2011).

In order to perform the statistical analysis, soils were divided into three groups (A, B and C) depending on pH values. The range of pH in groups A, B and C was 5.00 – 6.50 (n=49 samples), 6.55 – 7.50 (n=83 samples) and 7.51 – 7.97 (n=71 samples), respectively. Prevailing soil textures were Sandy Clay Loam and Clay Loam. ANOVA with LSD test for level of significance $p<0.05$ was used to identify significant differences between investigated chemical properties before and one year after the application of SS.

3. Results

The average chemical properties of the SS applied in 2013 are presented in Table 1. It is evident from Table 1, that 1 Mg of SS (on dry weight basis) adds 194 Kg Organic Matter, 321 Kg $CaCO_3$ and approximately 3 Kg N, 0.7 Kg P_2O_5 and 0.6 Kg K_2O, into the soil. SS contains low concentrations of metals and meets the European standards for agricultural use (CEC, 1986).

Table 1: Average chemical properties of the SS applied in 2013.

Parameter	Sewage Sludge	Kg added per Mg of sludge (d.w.)	Limits EU Directive 86/278/EC
Dry Matter (%)	55.5		
EC mScm^{-1}	17.8		
pH	8.2		
Organic Matter (%)	19.4	194	
$CaCO_3$ (%)	32.1	321	
NO_3^- (mgkg^{-1} d.w.)	2854	2.854†	
NH_4^+ (mgkg^{-1} d.w.)	55	0.055†	
Total N (mgkg^{-1} d.w.)	11520	2.2‡	
Olsen-P (mgkg^{-1} d.w.)	294	0.294†	
K (mgkg^{-1} d.w.)	493	0.493†	
DTPA extractable metals (mgkg^{-1} d.w.)			
Cu	10.7	0.011	
Zn	126.8	0.1268	
Pb	2.9	0.0029	
Cd	0.3	0.0003	
Ni	2.6	0.0026	
Cr	0.6	0.0006	
Total metal content (mgkg^{-1} d.w.)			
Cu	69	0.069	1000-1750
Zn	406	0.406	2500-4000
Pb	163	0.163	750-1200
Cd	1	0.001	20-40
Ni	26	0.026	300-400
Cr	281	0.281	500

†available forms

‡20% of the Total N is available in the first year of application (Sommers *et al*., 1981)

The statistical analysis of the average soil chemical parameters before and after the SS application on the three soil groups is presented in Table 2. According to Table 2, values of pH were statistically different before and after the application of SS in A and B but not in C soil group. In the acidic soil group A, pH was increased by an average of 0.81 units (15%) and in the neutral group B by 0.21 units (3%). In alkaline soil group C, pH remained almost the same without significant differences. The increase in pH is attributed to the high concentrations of $CaCO_3$ in the lime stabilized SS. The inherent buffering capacity of the soils in group C, maintained soil pH to the initial levels with an insignificant average increase of 0.03 units. Tsadilas *et al*. (1995) also observed an increase in an acidic soil pH with the use of SS. Akrivos *et al*. (2000) applied lime treated dewatered SS in alkaline soils and found that the increase in soil pH was no more than 0.2 units.

The concentration of $CaCO_3$, Ca_{exch} and Mg_{exch} increased in all three soil groups with significant differences before and after the application. $CaCO_3$ concentration was increased almost threefold in soil group A and by an average of 58% and 28% in soil groups B and C, respectively. Ca_{exch} was found higher than 2000 mgkg^{-1} in 196 out of 209 soil samples after SS application and Mg_{exch} showed an average increase of 28% in the soil samples.

Significant differences were found in EC values before and after one year of SS application in all three soil groups. In soil group A, EC increased from an average of 0.44 mScm^{-1} to 0.76 mScm^{-1}, in soil group B, from an average of 0.59 mScm^{-1} to 0.71 mScm^{-1} and in soil group C from an average of 0.47 mScm^{-1} to 0.64 mScm^{-1}.

Organic matter content did not show significant differences in all three soil groups after one year of SS application possibly due to i) the small amount of SS applied (~10 Mgha^{-1}) and ii) high rates of decomposition. Soil organic matter content after one year of SS application, was weakly correlated with applied SS amounts, with an r value of -0.02 (p=0.74). Mendoza *et al*. (2006) observed an increase in organic matter content with the application of 100 Mgha^{-1} SS by 1-2%, before crop establishment. However, the researchers reported that after plant growth, no significant changes were observed in this parameter with the initial soil status. This fact was attributed to possible qualitative transformations affecting organic matter. Merrington *et al*. (2003) pointed out that the degradation of the more easily degradable forms of SS organic matter by soil microbes is rapid and lasts several weeks, depending upon soil and environmental conditions.

Regarding metals concentration, Fe was reduced in soil groups A and B and was maintained the same in soil group C, Cd was maintained the same in soil groups A and B and decreased in soil group C, Cu showed no significant differences in the soil groups, while Mn, Co, Cr, Ni and Pb were reduced showing significant differences in all three soil groups after one year of SS application. Zinc which is one of the most abundant heavy metals in SS (Antoniadis, 2008; Mosquera-Losada *et al*., 2010) and is known to be amongst the most mobile heavy metals in the soil/plant system (Rigueiro-Rodriguez *et al*., 2012) was the only heavy metal that increased in the soil. As revealed by the statistical analysis, significant differences with the initial soil Zn concentration were found in the final concentrations in all three soil groups, were Zn was roughly doubled after a year of SS application.

Table 2: Comparison of the average chemical properties before (summer 2013) and after sludge application (summer 2014) in the three soil groups.

Parameter	Soil Group A (pH = 5.00-6.50)		Soil Group B (pH = 6.55-7.50)		Soil Group C (pH = 7.51-7.97)	
	Before	After	Before	After	Before	After
EC mScm^{-1}	0.44a[1]	0.76b	0.59a	0.71b	0.47a	0.64b
pH	5.77a	6.62b	7.10a	7.32b	7.72a	7.74a
Organic Matter (%)	1.52a	1.48a	1.69a	1.82a	1.62a	1.65a
$CaCO_3$ (%)	0.50a	1.85b	2.60a	4.10b	6.30a	8.07b
Ca_{exch}	1353a	>2000b	1888a	>2000a	>2000a	>2000a
Mg_{exch}	403a	486b	436a	534b	463a	621b
DTPA extractable metals (mgkg^{-1} d.w.)						
Fe	42.71a	32.90b	20.63a	16.41b	8.86a	9.50a
Mn	42.74a	29.35b	23.02a	16.48b	14.26a	11.17b
Cu	2.83a	2.48a	2.46a	2.16a	2.87a	2.35a
Cd	0.06a	0.06a	0.06a	0.06a	0.05a	0.04b
Co	0.44a	0.26b	0.25a	0.16b	0.16a	0.11b
Cr	0.23a	<0.01b	0.13a	<0.01b	0.14a	<0.01b
Ni	2.36a	1.46b	1.20a	0.84b	0.60a	0.49b
Pb	4.27a	2.37b	4.03a	2.39b	3.71a	2.26b
Zn	0.93a	1.92b	0.91a	1.57b	0.86a	1.53b

[1] Results of ANOVA. Different letters indicate statistically significant differences before and after the application of sewage sludge, at 0.05 confidence level.

4. Discussion

The results showed that DTPA-extractable metals were decreased over a one year period, with the exception of Zn. This indicates that in this study, sludge-borne metals and initial soil metals were possibly transferred from labile forms to more stable forms in the soil after the application of SS. This is in accordance with the findings of other researchers who used lime stabilized SS as a soil amendment (Seyhan and Erdincler, 2003; Cuevas *et al*., 2003). At present, there are two hypotheses concerning the bioavailability of sludge-borne heavy metals after SS application (McGrath *et al*., 2000; Pascual *et al*., 2004) i) sludge-borne heavy metals are maintained in chemical forms of low bioavailability by the inorganic components of the SS and ii) organic matter adsorbs heavy metals and thus it diminishes their toxicity symptoms.

A reduction in DTPA extractable metals is partially justified for the acidic and neutral soil groups due to the rise in pH caused by the lime stabilized sludge. However, strong retention of metals is often attributed to the inorganic fraction of SS. Furthermore, the strength and capacity of metal sorption by SS can be increased through the addition of lime (Merrington *et al*., 2003; Wong and Selvam, 2006). Carbonate forms sparingly insoluble solid phases through precipitation with many metals (Osman, 2013) and has been observed to account for the major portion of several metals in SS (Karapanagiotis *et al*., 1991). In this study, organic matter content was maintained the same, while DTPA extractable metals were reduced, over a one year period of SS application. This possibly indicates that the decomposition of organic matter in the soil did not control the availability of DTPA extractable metals and thus metals were strongly fixed in the inorganic fractions of the SS becoming more insoluble due to adsorption/precipitation processes. This reduction in metals concentration can not be attributed to leaching due to the fine texture of most studied soils and because it is well documented that leaching of heavy metals is limited (Han *et al*., 2001). Plant uptake of heavy metals which might have occurred, can not be held responsible for the significant reductions in trace elements and heavy metals. Other studies have reported limited heavy metal uptake by plants with the application of much higher rates of SS than the ones used in this study (Hormann *et al*., 1995; Jarausch–Wehrheim *et al*., 1996; Cuevas *et al*., 2003; Pascual *et al*., 2004).

5. Conclusions

In this study, lime stabilized SS from the WWTP of Thessaloniki Greece was applied as a single dose during November – December 2013 in 203 fields in the Thessaloniki Plain. It is concluded that i) the nutritional value of this SS is mainly limited to nitrogen, however the benefit could be increased in acidic soils, by providing favorable pH conditions for plant growth, through the addition of $CaCO_3$, ii) statistical analysis on the soils chemical properties, before and after one year period of SS application, showed that the application of this SS to soil as an amendment may be applied with no risk of increasing heavy metal bioavailability to phytotoxic levels and iii) the procedure can be an effective way of disposal of these residues.

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