ANALYSIS OF THE TOTAL COMPOSITION AND AVAILABILITY OF SOIL ELEMENTS AFTER MSW COMPOST APPLICATION

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1 INTRODUCTION

The steady loss of soil quality is a consequence of a progressive decrease in its organic matter content and soil macro- and micronutrients (Caridad, 2002). A controlled application of Municipal Solid Waste (MSW) compost can confer beneficial effects on the physical, chemical and biological soil properties by reducing the risk of soil pollution (Smith, 2009). Soil is affected by the organic amendment characteristics, hydrological conditions and management practices. The literature relating to the behavior and availability of heavy metals applied to the soils in compost trials is extensive and includes short and long-term investigations, chemical extraction and plant uptake studies and pot and field experimental work. Nevertheless, the amount of information specific to source-segregated compost is relatively limited (Smith, 2009). In order to obtain a more appropriate measure of the total concentration and availability of soil elements, it is necessary to take into account all the forms that these elements occur in the soil to assess their abundance and distribution, helping at the same time to characterize the soil. However, the analysis of soil elements can become very complex because of the often low concentrations (Ma et al., 1997) and it is very difficult to choose a suitable method for analyzing the total composition and the availability of the analyte after MSW compost addition due to the high diversity of soil elements and the wide variety of analytical methods. Recently, due to the adoption of spectrometry techniques many of these problems are being solved. Traditionally, the most common reagents used in the analysis of soil elements were a mixture of hydrofluoric acid and perchloric ($HF + HClO_4$) or regia water ($HNO_3 + HCl$). Baize (2000) indicated that the regia water gave lower values than the other two agents. This makes it extremely difficult to compare concentrations obtained by different extraction methods. The development of the technique of X-ray fluorescence is now an alternative to this traditional total analysis (Buurman et al., 1996). The main objective of this study was to establish the effect the addition of MSW compost had on the total composition and nutritional status of different agricultural soils from Galicia (NW Spain) and to compare different techniques for analysis of the total composition and availability of soil elements.

2 MATERIALS AND METHODS

2.1 Materials and Sampling

Experimental plots with or without MSW compost additions were established in several Galician agricultural soils, mainly belonged to the loam textural class. Twenty-nine plots without and nineteen with MSW compost addition (at a rate of 50 t ha^{-1}) were sampled in two years (2000-2001). Compost was just applied once in March at the start of the first year and soil samples were collected across the experimental period. Five soil subsamples were randomly taken in each plot from the surface horizon (0-20 cm depth) and were bulked for analyses. Composition and availability of soil elements, including macronutrients (P, K, Ca and Mg), micronutrients (Fe, Cu, Mn and Zn) and heavy metals (Cd, Cr, Ni and Pb) were determined using four analytical techniques.

2.2 Analytical Methods

The total analysis of soil elements was performed using two techniques, a semi-quantitative method, X-ray fluorescence (XRF), as well as a quantitative method, emission spectroscopy induced by argon plasma (ICP-MS). The availability of soil elements was determined using two extraction methods, the DTPA chelating agent and the Mehlich-3 acidic solution. Two analytical runs were carried out for each composite sample by each technique.

2.3 Statistical Analysis

Data analysis was performed by SPSS 17.0. The Student t-test was used to compare the differences between treatments (without and with MSW compost) and techniques (total composition, XRF vs. ICP-MS and availability of soil elements, DTPA vs. mehlich-3). No interaction was found between treatment and technique.

3 RESULTS AND DISCUSSION

According to the Spanish regulation (BOE, 1998) for the use of this type of organic amendment on agricultural soils, the quality of the MSW compost used experimentally in this trial can be categorized as good. However, the Pb values measured both by XRF (255 mg kg $^{-1}$) and ICP-MS (244 mg kg $^{-1}$) were very close to the maximum limit allowed (300 mg kg $^{-1}$) and should be addressed due to the risk of soil pollution.

3.1 Analysis of the total content of macronutrients (P, K, Ca and Mg) in the soil samples

No significant differences between treatments regarding the total content of macronutrients were observed (table 1). However, the concentrations of P, K and Ca measured by XRF and Ca determined by ICP-MS tended to be higher in the plots receiving MSW compost compared to those without. The values of P, K, Ca and Mg were significantly greater when analyzed by XRF than by ICP-MS for all plots because XRF was able to measure a higher quantity of these four macronutrients than ICP-MS.

TABLE 1 **Macronutrients P, K, Ca and Mg measured by XRF and determined by ICP-MS (g kg^{-1})**

Without compost	n	Mean	Dev.	Min.	Max	With compost	n	Mean	Dev.	Min.	Max.	Sig.[1]	Sig.[2]
XRF						**XRF**							
P_{total}	29	0.32	0.16	0.05	0.78	**P_{total}**	19	0.36	0.18	0.08	0.78	NS	***
K_{total}	29	2.28	0.70	1.35	4.41	**K_{total}**	19	2.33	0.67	1.58	4.01	NS	***
Ca_{total}	29	0.80	0.96	0.12	5.40	**Ca_{total}**	19	0.86	1.16	0.16	5.42	NS	**
Mg_{total}	29	1.10	0.31	0.43	1.66	**Mg_{total}**	19	0.98	0.32	0.53	1.57	NS	***
ICP-MS						**ICP-MS**							
P_{total}	29	0.11	0.05	0.03	0.27	**P_{total}**	19	0.11	0.07	0.02	0.27	NS	***
K_{total}	29	0.41	0.16	0.10	0.73	**K_{total}**	19	0.34	0.18	0.10	0.63	NS	***
Ca_{total}	29	0.33	0.66	0	3.59	**Ca_{total}**	19	0.41	0.86	0.02	3.91	NS	**
Mg_{total}	29	0.65	0.24	0.20	1.25	**Mg_{total}**	19	0.63	0.26	0.17	1.10	NS	***

[1]Sig. treatment= without vs. with compost (NS, Not significant differences; * P<0.05; **P<0.01; ***P<0.001).

[2]Sig. technique = XRF vs. ICP-MS (NS, Not significant differences; * P<0.05; **P<0.01; ***P<0.001).

3.2 Analysis of the total content of micronutrients (Fe, Cu, Mn and Zn) in the soil samples

No significant differences between treatments regarding the total content of micronutrients were found (table 2). The total amount of all these four micronutrients varied over a large range due to the heterogeneity of the MSW compost used experimentally or an unequal distribution of the MSW compost compounds over the plots. However, this variation was not higher than for the macronutrients. These results illustrated the difficulty of studying, over a short term period, the effect of compost action on the soil micronutrients content.

TABLE 2 **Micronutrients Fe, Cu, Mn and Zn measured by XRF and determined by ICP-MS (mg kg^{-1}).**

Without compost	n	Mean	Dev.	Min.	Max.	With compost	n	Mean	Dev.	Min.	Max.	Sig.[1]	Sig.[2]
XRF						**XRF**							
Fe_{total}	29	44094	7583	24450	61330	**Fe_{total}**	19	42474	7996	28000	59000	NS	***
Cu_{total}	29	67	17	22	110	**Cu_{total}**	19	65	14	28	84	NS	***
Mn_{total}	29	1100	256	420	1610	**Mn_{total}**	19	1049	247	640	1800	NS	***
Zn_{total}	29	156	47	50	270	**Zn_{total}**	19	151	42	80	280	NS	***
ICP-MS						**ICP-MS**							
Fe_{total}	29	33862	5027	20000	34000	**Fe_{total}**	19	30211	7714	13000	39000	NS	***
Cu_{total}	29	34	13	4	73	**Cu_{total}**	19	30	10	3	46	NS	***
Mn_{total}	29	771	202	333	1189	**Mn_{total}**	19	743	256	400	1542	NS	***
Zn_{total}	29	94	31	30	150	**Zn_{total}**	19	86	33	31	172	NS	***

[1]Sig. treatment= without vs. with compost (NS, Not significant differences; * P<0.05; **P<0.01; ***P<0.001).

[2]Sig. technique = XRF vs. ICP-MS (NS, Not significant differences; * P<0.05; **P<0.01; ***P<0.001).

The values of Fe, Cu, Mn and Zn were significantly greater when analyzed by XRF than by ICP-MS for all plots because ICP-MS was not able to release the elements contained in the silicate formations or from the minerals.

3.3 Analysis of the total content of heavy metals (Cr, Ni and Pb) in the soil samples

No significant differences between treatments regarding the total content of heavy metals were observed (table 3). The values of Cr, Ni and Pb were significantly greater when analyzed by XRF than by ICP-MS for all plots. The average values of these three heavy metals were approximately twice higher by XRF than by ICP-MS.

TABLE 3 **Heavy metals Cr, Ni and Pb measured by XRF and determined by ICP-MS (mg kg^{-1})**

Without compost	n	Mean	Dev.	Min.	Max.	With compost	n	Mean	Dev.	Min.	Max.	Sig.[1]	Sig.[2]
XRF						**XRF**							
Cr_{total}	29	113	57	40	310	**Cr_{total}**	19	102	46	13	155	NS	***
Ni_{total}	28	58	25	30	125	**Ni_{total}**	19	53	23	8	91	NS	***
Pb_{total}	5	43	12	38	56	**Pb_{total}**	18	43	24	38	103	NS	***
ICP-MS						**ICP-MS**							
Cr_{total}	29	48	27	40	260	**Cr_{total}**	19	45	27	13	143	NS	***
Ni_{total}	29	28	19	27	115	**Ni_{total}**	19	25	16	8	81	NS	***
Pb_{total}	29	25	10	25	103	**Pb_{total}**	19	25	12	13	63	NS	***

[1]Sig. treatment= without vs. with compost (NS, Not significant differences; * P<0.05; **P<0.01; ***P<0.001).

[2]Sig. technique = XRF vs. ICP-MS (NS, Not significant differences; * P<0.05; **P<0.01; ***P<0.001).

The soil analysis also revealed that the total levels of some elements like Cu, Zn, Cr and Ni, in the Galician agricultural soils studied in this trial, are close to the Dutch restrictions implemented in 1987 (Ma et al.,1997).

3.4 Analysis of the available micronutrients (Fe, Cu, Mn and Zn) in the soil samples

There were no significant differences between treatments for the availability of micronutrients measured by DTPA (table 4). However, a significantly (P<0.001) higher content of Fe, Cu and Mn determined by Mehlich-3 was found in the plots with MSW compost addition. Moreover, the heavy metal Zn measured by the Mehlich-3 method tended to exhibit higher concentrations in the MSW compost plots.

No significant differences were found between techniques for Fe, Mn and Zn. However, a trend towards a higher amount extracted by DTPA was found in the plots without MSW compost for these three micronutrients while the Mehlich-3 method showed the opposite trend. For Cu, a significantly (P<0.05) higher concentration was obtained using the DTPA chelating agent in the plots without MSW compost while in the plots with MSW compost addition higher concentrations of Cu were found using the Mehlich-3 method. These results indicate that it is why it is very difficult to give coherent recommendations regarding the use of DTPA or Mehlich-3 extraction for these soils and further studies are required.

The decline in the relative availability of Cu and Zn measured by DTPA in amended soils may be explained due to the influence of the compost matrix on the sorption of metals compared to the non-amended. Soil types with a strong affinity for metal sorption, e.g. soils with high clay content, may be less responsive to the effects of pH (Smith, 2009) on metal availability and other mechanisms may have a more dominant role in metal behavior.

TABLE 4 **Micronutrients Fe, Cu, Mn and Zn measured by DTPA and determined by Mehlich-3 (mg kg^{-1})**

Without compost	n	Mean	Dev.	Min.	Max.	With compost	n	Mean	Dev.	Min.	Max.	Sig.[1]	Sig.[2]
DTPA						**DTPA**							
$Fe_{available}$	29	97.1	46.3	31.5	207.8	**$Fe_{available}$**	12	104.4	69.9	44.2	274.8	NS	NS
$Cu_{available}$	29	3.8	3.5	0.1	15.2	**$Cu_{available}$**	12	2.6	1.4	0.9	6.1	NS	*
$Mn_{available}$	29	34.2	25.0	5.0	98.4	**$Mn_{available}$**	12	43.2	31.3	9.0	112.8	NS	NS
$Zn_{available}$	29	7.8	10.6	0.7	49.8	**$Zn_{available}$**	12	4.2	3.2	0.8	12.6	NS	NS
Mehlich-3						**Mehlich-3**							
$Fe_{available}$	29	93.2	82.4	18.0	286.2	**$Fe_{available}$**	12	232.4	77.1	116.2	360.2	***	NS
$Cu_{available}$	29	1.6	1.3	0	4.6	**$Cu_{available}$**	12	3.6	2.4	1.3	10.2	***	*
$Mn_{available}$	29	16.3	26.6	1.4	127.0	**$Mn_{available}$**	12	60.2	33.5	25.6	141.9	***	NS

$Zn_{available}$	29	4.1	5.1	0	24.7	**$Zn_{available}$**	12	7.4	7.7	1.1	24.6	NS	NS

[1]Sig. treatment= without vs. with compost (NS, Not significant differences; * P<0.05; **P<0.01; ***P<0.001).

[2]Sig. technique = XRF vs. ICP-MS (NS, Not significant differences; * P<0.05; **P<0.01; ***P<0.001).

3.5 Analysis of the available heavy metals (Cd, Cr, Ni and Pb) in the soil samples

The analysis of the heavy metals (Cd, Ni and Pb) using DTPA and Mehlich-3did not show any significant differences between treatments (table 5). However, the concentrations of Cd and Pb tended to be higher in the MSW compost plots compared to those without. For Cr, a significantly greater concentration was obtained using DTPA in the plots without MSW compost while using Mehlich-3 higher amounts of Cr were found in the compost plots.

Mehlich-3 extracted a significantly (P<0.001) higher amount of Cr than DTPA in both treatments. However, for Ni (P<0.05) and Pb (P<0.001) the contrary result was obtained with higher concentrations using DTPA than Mehlich-3. For Cd, no differences were found at all between treatments although a higher amount of this heavy metal was extracted using DTPA than by Mehlich-3. These results are in line with a research reported by Caridad (2002) who recognized that it is not possible to recommend the use of DTPA or Mehlich-3 extraction for samples of widely variable soils because of the important role of physical and chemical soil properties.

TABLE 5 **Heavy metals Cd, Cr, Ni and Pb measured by DTPA and determined by Mehlich-3 (mg kg^{-1}).**

Without compost	n	Mean	Dev.	Min.	Max.	With compost	n	Mean	Dev.	Min.	Max.	Sig.[1]	Sig.[2]
DTPA						**DTPA**							
$Cd_{available}$	29	0.06	0.06	0	0.20	**$Cd_{available}$**	12	0.07	0.04	0	0.15	NS	NS
$Cr_{available}$	29	0.08	0.04	0	0.10	**$Cr_{available}$**	12	0.01	0.02	0	0.13	***	***
$Ni_{available}$	29	0.87	1.37	0.03	4.62	**$Ni_{available}$**	12	0.46	0.19	0	2.06	NS	*
$Pb_{available}$	29	1.98	1.31	0.19	6.17	**$Pb_{available}$**	12	2.47	0.88	0	4.50	NS	***
Mehlich-3						**Mehlich-3**							
$Cd_{available}$	29	0.03	0.05	0.02	0.16	**$Cd_{available}$**	12	0.07	0.09	0	0.24	NS	NS
$Cr_{available}$	29	0.11	0.06	0	0.07	**$Cr_{available}$**	12	0.21	0.16	0	0.44	**	***
$Ni_{available}$	29	0.28	0.58	0.27	5.10	**$Ni_{available}$**	12	0.20	0.23	0	2.59	NS	*
$Pb_{available}$	29	0.51	0.96	1.26	4.22	**$Pb_{available}$**	12	0.56	1.02	0	3.33	NS	***

[1]Sig. treatment= without vs. with compost (NS, Not significant differences; * P<0.05; **P<0.01; ***P<0.001).

[2]Sig. technique = XRF vs. ICP-MS (NS, Not significant differences; * P<0.05; **P<0.01; ***P<0.001).

4 CONCLUSIONS

No differences between treatments in the total content of macro- and micronutrients and heavy metals measured by XRF and ICP-MS were found. XRF determined a higher quantity of soil elements than ICP-MS in all plots studied. However, a significantly higher content of available Fe, Cu, Mn and Cr measured by Mehlich-3 was found in the MSW compost plots. Mehlich-3 extracted a significantly higher content of Cr than DTPA in both treatments. For Cu, Ni and Pb the contrary result was obtained with higher concentrations by DTPA. It was not possible to recommend the use of DTPA or Mehlich-3 extraction for samples of mixed widely variable soils.

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REFERENCES

Baize D 2000. II Sistema francese di referenziazione dei suoli “Referentiel Pedologique”. Institut National de la Recherche Agronomique (ed.). Paris, France. 356 p.

BOE (Boletín Oficial del Estado) 1998. Orden de 28 de mayo de 1998 sobre fertilizantes y afines. Ministerio de la Presidencia (ed.). Madrid, España. Núm. 131, 18028-18078 p.

Buurman P, van Lagen B, Velthorst E J 1996. Manual for soil and water analysis. Backhuys Publishers (ed.). Leiden, The Netherlands. 120 p.

Caridad R 2002. Contenido de macro-, micronutrientes, metales pesados y otros elementos en suelos naturales de São Paulo (Brasil) y Galicia (España). Universidade da Coruña (ed.). A Coruña, España. 574 p.

Ma L Q, Tan F, Harris W G 1997. Concentrations and distributions of eleven metals in Florida soils. Journal of Environmental Quality 26, 769-775.

Smith S R 2009. A critical review of the bioavailability and impacts of heavy metals in municipal solid waste composts compared to sewage sludge. Environmental International 35(1), 142-156.