Article

Effect of Particle Size on Compost Analysis by Portable X-ray Fluorescence

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Featured Application: Portable X-ray fluorescence (pXRF) could be used more and better to analyze compost. The analysis could be carried out cheaply and quickly, but the measurement procedure must be standardized.

Abstract: Portable X-ray fluorescence (pXRF) could be more widely used for analyzing organic amendments, because it allows for a fast and low-cost analysis and is easy to use, among other operational advantages. However, the heterogeneity of these materials causes deviations in the measurements made. In the present study, three composts different in their origin (municipal solid waste (MSW), sewage sludge, and alperujo (i.e., olive oil manufacturing) waste) and composition were used. The effect that the laboratory grinding process had on the results of their elemental analysis conducted with pXRF was studied, as well as the elemental composition of the compost granulometric fractions. The grinding process of the fractions larger than 0.5 mm caused higher concentration readings for the elements Si (up to 47%), Ti (up to 30%), Al (up to 27%), K (up to 26%), P (up to 24%), V (up to 18%), and Pb (up to 16%) and lower readings for Zn (up to -41%) and Cu (-64%) in the ground samples. The differences depended on the type of compost. However, in the complete compost samples, the grinding caused lower reductions: -34% in the Cu concentration of the MSW compost, -20% in the Zn concentrations of the MSW compost and the alperujo compost, and a 15.2% increase in the P concentration of the MSW compost. For most of the elements, grinding did not cause significant differences. Since several of the elements that presented wide variations are essential for the characterization of compost, it is recommended that in order to carry out measurements with this technique, a sample preparation process is carried out that guarantees its homogeneity.

Keywords: heavy metals analysis; organic amendments; plant nutrients; pXRF; sample grinding

1. Introduction

Portable X-ray fluorescence spectrometry (pXRF) has undergone significant technological improvements and has been applied extensively [1,2], including in archaeology, geology and mining, and environmental sciences as well as in the elemental analysis of numerous materials (alloys, rocks, soils, and sediments, among others). This technique has several advantages over other laboratory analysis procedures for the determination of the content of elements with an atomic number $Z > 12$, including its speed (results in minutes), unnecessary sample preparation, no generation of polluting laboratory waste, portability, ease of use, and competitive price [3].

Despite these advantages, this technique has been little used in the elemental analysis of composts and other organic amendments, such as manure or sewage sludge [3]. Standardized laboratory procedures for determining plant nutrients and heavy metal contents

and other properties in these materials are generally tedious. They involve fine-grained grinding of the sample (normally less than 0.5 mm), which guarantees the homogeneity and reproducibility of the results. The sample is then digested in strong acids, such as aqua regia (EN 13650:2001 [4], ISO 54321 [5], US EPA methods 3050B and 3051 [6]).

The granulometry of compost particles can affect the analysis of trace elements and plant nutrients by pXRF in two ways. On the one hand, composts are nonhomogeneous materials, made up of particles of different sizes and nature. Various authors have shown that the distribution of trace elements and nutrients varies among the different granulometric fractions, with a tendency for heavy metals to accumulate in the finer fractions [7–10]. On the other hand, the measurement window of the pXRF instruments covers a few square millimeters. The information depth (that is, the thickness of the sample matrix from which the secondary radiation will return to the detector) is of the order of a few millimeters and is specific to each element. Laperche and Lemière [2] indicate that for a soil matrix, the Ca response is obtained from the first 100 μm of the sample, while for Ba, the response is obtained from 2 cm. Therefore, in the case of coarse particulate materials, such as compost, the results of a scan can be very dependent on the particles of the materials that have been focused by the instrument.

It is a recognized fact that the greater or lesser the homogeneity/heterogeneity of the material greatly influences the dispersion of the results obtained [11]. Applying pXRF to waste samples, Havukainen et al. [12] concluded that the technique works for qualitative characterization and requires homogeneous, not very wet, and small particle size samples. However, the possible influence of the granulometry of the samples on the pXRF results, in the compost studies carried out to date with the exception of [10], has been scarcely taken into account. Samples of composts or other organic amendments have usually been analyzed without any previous treatment or, alternatively, after a previous grinding process, such as that necessary to carry out analyses by the aqua regia wet method.

The particle size is a physical characteristic of the sample that can be manipulated by the operator by grinding the sample. However, the grinding process is tedious, inadequate if rapid, and a field analysis is to be carried out; in addition, as indicated above, it can affect the XRF results.

In the present study, the results of an elemental analysis using pXRF in the granulometric fractions of three composts were compared, as well as the effect produced by the milling process on the pXRF readings. Three kinds of composts with different origins and compositions were used: a compost of municipal solid waste (MSW) from a selective collection, a compost of sewage sludge, and a compost from the agrifood industry for the manufacture of olive oil.

The results of the study will make it possible to elucidate to what extent a pretreatment of the samples is necessary to ensure their homogeneity to accurately determine the contents of various elements that are essential for the agronomic and environmental characterization of a compost.

2. Materials and Methods

2.1. Compost Types

Three types of compost were chosen for this study, because they were different in their composition, origin, and characteristics, as well as being abundant.

The first compost (hereinafter sewage compost) was prepared with a mixture of sewage sludge and pruning waste from urban gardening. The sewage sludge came from the Copero plant (Sevilla, southern Spain), and the composting was carried out at a sludge:pruning ratio of 1:3 (w/w) in turned piles for a period of 4 months. It was then air-dried and kept in cold storage for three years before being used in this study [13]. Three subsamples were taken from each of the three bags of material that were available. The sewage compost was supplied by the company EMASESA (Sevilla, Spain).

The second was a compost of source-separated municipal solid waste that is, biowaste compost, hereinafter MSW compost. It was subjected to composting for 3 months plus

two months of maturation, and it was sieved through a 6 mm sieve at the Montemarta-Cónica composting plant located in Alcalá de Guadaíra, Sevilla. It was a batch of compost corresponding to the initial stages of the implementation of the selective collection in the city of Seville as a result of European directives. Being an experimental batch, it did not undergo the usual refining processes and contained a certain proportion of glass fragments that were manually separated in the laboratory before use. Three samples were taken from different positions from an available 50 kg bag.

The third was compost from olive oil manufacturing waste, known as "alperujo". Alperujo contains the solid parts of the olive, such as the pit, the mesocarp, and the skin; process water; and fatty remains. The alperujo compost used in this study was taken from the company Aceite Las Valdesas (Puente Genil, Córdoba). The samples were taken from a one-year-old compost pile. Three samples were taken at three different locations from a 50 m long pile.

The general chemical properties of the three composts and their granulometry are shown in Table 1.

Table 1. Compost characteristics (±standard deviation).

		Compost Type		
		Sewage	**MSW**	**Alperujo**
pH		6.36 ± 0.05	7.39 ± 0.17	8.13 ± 0.02
E.C. [1]	dS m^{-1}	1.44 ± 0.30	3.10 ± 0.19	3.57 ± 47
OM [2]	g kg^{-1}	310 ± 18	457 ± 47	726 ± 11
kj-N [3]	g kg^{-1}	18.5 ± 10	17.9 ± 1.8	19.0 ± 1.2
C/N ratio		9.7 ± 0.7	14.8 ± 1.2	22.2 ± 1.7
>5 mm	%	0.9 ± 0.1	2.0 ± 0.7	6.4 ± 1.2
2–5 mm	%	6.8 ± 1.2	29.8 ± 2.0	32.4 ± 0.9
0.5–2 mm	%	34.9 ± 5.2	39.2 ± 1.5	51.2 ± 0.7
<0.5 mm	%	57.5 ± 4.1	29.0 ± 1.4	10.1 ± 2.3

[1] E.C.: electrical conductivity, 1:5 w/vol extract; [2] OM: organic matter content; [3] kj-N: Kjeldahl nitrogen.

2.2. Compost Analyses

The general chemical properties (i.e., pH, electrical conductivity, organic matter content, Kjeldahl-Nitrogen content, and C/N ratio) were determined following the standard European procedures for soil improvers and growing media. Extractable aqua regia elements were determined following the standard procedure EN 13650:2001 [4]. After, the acid extraction elements were determined by inductively coupled plasma combined with optical emission spectroscopy (ICP-OES) (VARIAN 720-ES, Agilent Technologies, Santa Clara, CA, USA).

The element concentrations were determined by pXRF by means of the analyzer Niton XL3t 950s GOLDD+ XRF (Thermo Scientific Inc., Billerica, MA, USA) mounted on its laboratory stand. The samples were placed in an XRF sample cup (model SC-4331, 26 mm internal diameter, 24 mm height, Premier Lab Supply Inc., Port St. Lucie, FL, USA) capped with a 4 μm propylene film (model 240255, 63 mm diameter, Premier Lab Supply Inc., Port St. Lucie, FL, USA). The sample cup was centered in the window of the laboratory stand and scanned in triplicate in each of the precalibrated soil and mining modes. For each scan, the sample container was repositioned to focus on the different sample aliquots. Then, only the average of the three repetitions in each mode was used. The analysis time for each scan was 60 s for the soil mode and 90 s for the mining mode.

The soil mode is based on Compton normalization and is often used for the scanning and detection of metallic elements [14] at low concentrations (<1% or 10 g kg^{-1}). Depending on a sufficient concentration in the sample (that is, above the limit of quantification) readings for the following elements can be obtained in the soil mode: Mo, Zr, Sr, Rb, Pb, As, Zn, Cu, Ni, Fe, Mn, Cr, V, Ti, Sc, Ca, K, S, Ba, U, Th, Au, Se, Co, Hg, W, Cs, Te, Sb, Sn, Cd, Ag, and Pd.

The mining mode is based on the fundamental parameter calibration, and it is recommended for high concentrations (>1% or 10 g kg^{-1}) and quantification [15]. In the mining mode, readings can be obtained for the following elements: Mo, Zr, Sr, Rb, Pb, As, Zn, Cu, Ni, Fe, Mn, Cr, V, Ti, Ca, K, S, Ba, Sn, Ag, Nb, U, Th, Au, Se, Co, W, Sb, Cd, Pd, Bi, Al, P, Si, Cl, Mg, and Bal. The parameter called "Bal" refers to the balance, the amount of signal the instrument is unable to attribute to an element (Bal + element readings = 100%, or 10^3 g kg^{-1} or 10^6 mg kg^{-1}).

The analyzer has an X-ray tube and a Ag anode, operated at 50 keV, 200 μA, and 2 W, with a geometrically optimized large Si drift detector (GOLDD). More information regarding the instrument can be found on the manufacturer's website [16]. Detailed information regarding the technique can be found in [15,17].

The sediment sample SdAR-M2, which is a blended material produced by the US Geological Survey [18], was repeatedly analyzed each working day to check the performance of the analyzer.

2.3. Particle Size Effects on the pXRF Readings

The compost samples initially used in the laboratory were approximately 150–200 g. Three replicates were used per type of compost.

The compost samples were dried in an oven at 105 °C for two days, carefully homogenized, and an aliquot of the integral sample was scanned in the pXRF instrument. Then, their granulometric fractions were separated using 5, 2, and 0.5 mm sieves. Thus, the following fractions were obtained: >5, 2–5, 0.5–2, and <0.5 mm. Each size fraction was weighed and carefully homogenized, and an aliquot was used to fill the XRF sample cup and scanned in the pXRF instrument.

Each particle size fraction (except the <0.5 mm fraction) was ground in a mill (IKA MF 10.1, IKA-Werke, Staufen, Germany) equipped with a 0.5 mm sieve. The ground samples were homogenized, the measurement capsules were filled, and the pXRF readings were carried out again with triplicate scanning. To perform the scan of the ground integral sample, it was recomposed from the ground fractions, homogenized, and measured again by pXRF. In this way, the maximum similarity of this ground sample with its original was guaranteed, since otherwise, when separating the fractions, it would have been necessary to use two different aliquots.

2.4. Statistical Procedures

The statistical analyses were carried out with IBM© SPSS© Statistics version 27 (SPSS, Chicago, IL, USA). The comparison of the means of the samples with and without grinding for the integral sample and for the granulometric fractions was carried out using a *t*-test of the paired samples. An analysis of variance (ANOVA) and Tukey's test were used to compare the concentration of an element between the various granulometric fractions. Previously, the normality and homoscedasticity of the data were checked. A probability level of $p = 0.05$ was used throughout the study.

To estimate the variability of the three composts used, the relative percentage range (RPR) was calculated from the aqua regia concentrations given in Table 2, according to the formula

$$\text{RPR}_i = (C_{i\,max} - C_{i\,min}) \times 100/((C_{i\,max} + C_{i\,min})/2) \tag{1}$$

where $C_{i\,max}$ and $C_{i\,min}$ are the maximum and minimum concentrations of element I of the three compost.

Table 2. Extractable aqua regia contents of the composts (mg kg^{-1} $\pm$ standard deviation).

	Sewage	MSW	Alperujo
V	34.6 $\pm$ 1.7	10.1 $\pm$ 1.6	7.97 $\pm$ 0.48
As	9.06 $\pm$ 2.04	0.383 $\pm$ 0.148	5.18 $\pm$ 0.49
Ba	150 $\pm$ 6	118 $\pm$ 46	31.7 $\pm$ 2.4
Cd	0.88 $\pm$ 0.10	6.97 $\pm$ 1.26	<0.1
Cr	61.3 $\pm$ 8.4	202 $\pm$ 103	20.7 $\pm$ 2.4
Cu	173 $\pm$ 3	175 $\pm$ 13	68.7 $\pm$ 4.1
Mn	441 $\pm$ 17	282 $\pm$ 30	122 $\pm$ 17
Ni	26.5 $\pm$ 3.0	93.0 $\pm$ 45.0	8.96 $\pm$ 1.27
Pb	42.6 $\pm$ 8.7	82.2 $\pm$ 5.0	2.26 $\pm$ 0.79
Sr	132 $\pm$ 4	150 $\pm$ 7	66.2 $\pm$ 5.1
Sn	17.3 $\pm$ 1.5	48.1 $\pm$ 3.6	1.3 $\pm$ 0.5
Zn	507 $\pm$ 15	552 $\pm$ 19	34.1 $\pm$ 1.4
P $\times$ 10^{-3}	16.2 $\pm$ 0.6	8.88 $\pm$ 0.95	1.87 $\pm$ 0.15
K $\times$ 10^{-3}	4.37 $\pm$ 0.11	8.46 $\pm$ 0.48	13.4 $\pm$ 0.5
Ca $\times$ 10^{-3}	42.9 $\pm$ 1.1	78.9 $\pm$ 3.1	47.6 $\pm$ 0.5
Mg $\times$ 10^{-3}	13.2 $\pm$ 0.5	8.29 $\pm$ 1.55	2.50 $\pm$ 0.16
S $\times$ 10^{-3}	13.2 $\pm$ 1.2	5.00 $\pm$ 0.14	2.00 $\pm$ 0.07
Al $\times$ 10^{-3}	18.0 $\pm$ 0.4	9.66 $\pm$ 0.69	6.54 $\pm$ 0.47
Fe $\times$ 10^{-3}	40.5 $\pm$ 1.3	22.3 $\pm$ 1.5	4.70 $\pm$ 0.39

3. Results and Discussion

3.1. Compost Characteristics

The general characteristics of the composts shown in Table 1 indicate that they were different from each other, having variable contents of organic matter between 310 and 726 g kg^{-1} and different granulometric compositions. The sewage compost presented a prevalence of fine particles, with more than 92% of its particles being smaller than 2 mm. The MSW compost presented a balanced granulometric distribution of the size fractions 2–5, 0.5–2, and <0.5 mm. The alperujo compost presented a predominance of intermediate particles 0.5–2 mm with few fine particles <0.5 mm.

Table 2 shows the aqua regia soluble elemental contents of the composts. Relating to the different origins and nature of the three composts, wide variations in the composition can be observed. The highest concentrations of V, As, Ba, Mn, P, Mg, S, Al, and Fe were found in the sewage compost. The highest concentrations of Cd, Cr, Cu, Ni, Pb, Sr, Sn, Zn, and Ca were found in the MSW compost. The concentrations of Cd and Ni in this compost exceeded the tolerance limits in force in Europe for soil improvers (2 and 50 mg kg^{-1}, respectively) and growing media (1.5 and 50 mg kg^{-1}, respectively) [19]. The alperujo compost generally showed the lowest concentrations of trace elements and heavy metals, which are indicators of anthropogenic contamination, such as Cd, Cr, Cu, Ni, Pb, Sn, and Zn, and the highest concentration of K, a plant nutrient from the olive. The concentrations of the elements Cd, Hg, Ni, Pb, and As, which are considered in the European legal regulation, both in the alperujo compost and in the sewage compost did not exceed the tolerance limits in force in Europe.

It is worth noting here that the aqua regia procedure and XRF do not necessarily have to provide the same element concentrations because XRF measures total contents while aqua regia does not dissolve the entire sample (these are often referred to as pseudo-total contents), and this depends on the characteristics of the sample (for example of elements that are associated with silicates) [3,20].

As a measure of the variability among the three composts used, the RPR was 194% for Cd, 189% for Sn and Pb, 184% for As, 177% for Zn, 165% for Ni, 163% for Cr, 159% for Fe, 147% for S, 136% for Mg, 130% for Ba, 125% for V, 113% for Mn, and 102% for K. Only for the elements Al (93%), Cu (87%), Sr (78%), and Ca (59%), was the RPR less than 100%.

The choice of these three composts for carrying out this study is supported by their different origins and their varied characteristics.

3.2. Stability and Performance of the pXRF Analyzer

The concentrations determined with pXRF in the certified reference material (CRM) SdAR-M2 are shown in Table 3. During the development of the experiments, this sediment sample was analyzed 21 times (12 and 9) in two periods of time more than one year apart.

Table 3. Performance of the instrument: variations in daily measurements (N = 21) of the certified reference material sediment SdAR-M2.

	Certified Value, mg kg^{-1}	Average Value, mg kg^{-1}	Recovery, %	Minimum Recovery, %	Maximum Recovery, %	Average RD [1], %
Ag	15	19.8	131.8	86.3	178.6	32.9
As	76	78.2	102.9	73.8	131.7	11.8
Ba	990	837	84.5	78.2	91.8	15.5
Cd	<10	15.3	-	75.0 [2]	149.8 [2]	37.6 [2]
Cr	49.6	53.7	108.3	73.1	151.1	19.1
Cu	236	222	93.9	75.8	105.8	6.6
Mn	1038	843	81.2	74.9	93.4	18.8
Ni	48.8	63.6	130.4	77.0	170.3	33.3
Pb	808	812	100.6	96.1	104.8	1.8
Rb	149	135	90.5	86.5	94.2	9.5
S	970	1117	115.2	77.4	156.5	18.3
Sb	107	98.9	92.4	83.4	110.0	8.6
Sr	144	142.2	98.8	92.8	103.1	1.8
Th	14.2	15.7	110.3	74.4	142.2	34.7
Ti	1798	1360	75.6	65.8	83.3	24.4
Zn	760	713	93.9	87.3	99.5	6.1
K × 10^{-3}	41.5	37.1	89.3	76.6	95.4	10.7
[3] Fe × 10^{-3}	18.4	18.4	99.8	97.5	103.0	5.0
[3] Ca × 10^{-3}	6.00	5.62	93.6	87.8	96.9	10.0
[3] Si × 10^{-3}	343	279	81.4	73.6	93.4	21.8

[1] Average value of the absolute relative deviations; [2] relative deviations calculated in relation to the average value; [3] for these elements, measurements were conducted in the precalibrated mining mode; for the rest of the elements, the measurements were performed with the precalibrated soil method.

The concentrations of the elements Cd, Cr, Cu, Mn, Ni, Sr, Zn, and Fe in the CRM were of the same order of magnitude as they were in the compost samples.

The average recoveries for the elements As, Cr, Cu, Pb, Rb, Sb, Sr, Th, Zn, Fe, and Ca were ±10% of the certified values. The average recoveries for the elements Ba, Mn, S, Th, K, and Si were between ±10% and ±20% of the certified values. Only for the elements Ag, Ni, and Ti were the recoveries greater than ±20% of the certified values, and in the case of Ag and Ni, this deviation was due to the proximity of their concentrations in the CRM to the detection limit of the instrument. The USEPA method for soil and sediment analysis by pXRF states that the measured value for the analyte in the CRM samples should be within ±20% of the true value for the check to be acceptable [21].

Similarly, the average of the absolute relative deviations (RDs) was less than 10% for the elements Cu, Pb, Rb, Sb, Sr, Zn, Fe, and Ca, indicating their high instrument stability. The mean RD was between 10 and 20% for the elements Ba, Cr, Mn, S, and K, indicating the acceptable instrument stability of these elements, while the RD was greater than 20% for Ag, Cd, Ni, Th (these four elements had values close to the detection limit), Ti, and Si. It is worth noting here that Ti and Si are two elements rarely considered in compost studies, because they are nonessential nutrients for plants and are nontoxic.

3.3. Influence of the Particle Size on the Elemental Concentration Determined by pXRF Fractions

The concentrations of several elements in the different particle size fractions (after milling them) of the three composts are shown in Figure 1. As can be seen in the figure, important variations were found for all of the elements between the different size fractions.

As a rule of thumb, the concentrations of the elements included in Figure 1 were higher in the finer fractions, with the exception of K, Cu, and S in the alperujo compost.
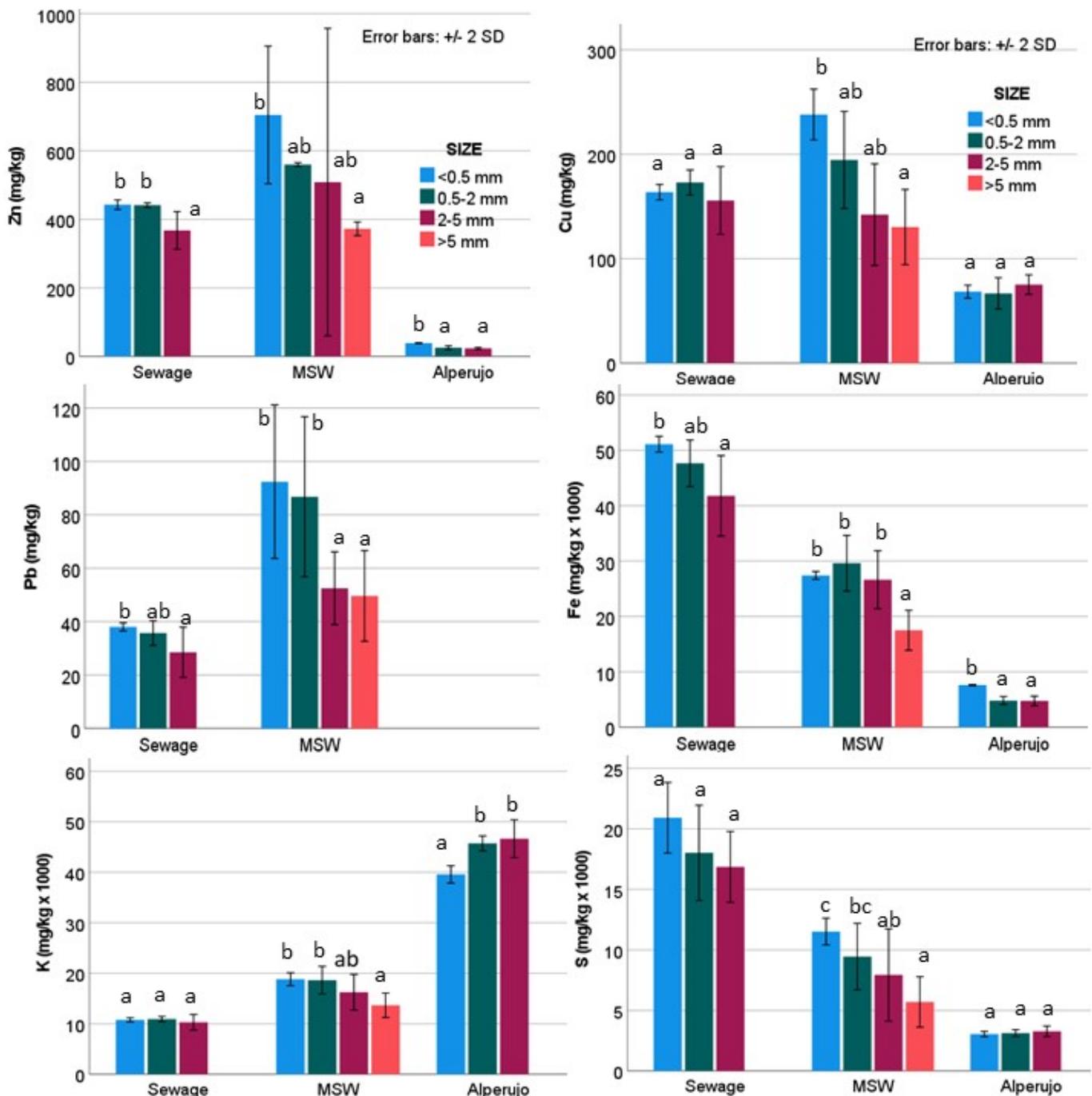
Figure 1. Concentrations of various elements in the ground granulometric fractions of the sludge compost, MSW compost, and alperujo compost. Bars with the same lower letter do not differ statistically according to Tukey's test ($p < 0.05$).

The most remarkable differences were in the MSW compost in which the concentrations of Zn, Cu, Pb, and S almost doubled in the finer fraction (<0.5 mm) compared to the coarse fractions (2–5 and >5 mm). In this compost, the concentrations of Fe and K were also higher in the fine fractions, although the differences were less significant. These results are in agreement with previous studies [8,9] carried out on MSW composts.

In the sewage compost, higher concentrations of Zn, Pb, Fe, and S were observed as the fraction was finer, although the differences were less notable than in the MSW compost.

In the alperujo compost, higher concentrations of Zn and Fe were observed in the finer fraction (<0.5 mm) and a higher concentration of K in the coarser fractions, greater than 0.5 mm.

The reasons that justify these variations may be different and specific for each compost depending on its origin and nature. It is a known fact that in soils, the concentrations of trace elements increase as the particle size decreases, which is associated with the adsorption of these elements by the clays [22,23]. In addition, in compost, finer fractions have been shown to accumulate heavy metals [9,10]. In previous studies, the size fractionation highlighted Cd, Cu, Zn, and Pb accumulation in the fine-sized fractions, while Cr and Ni accumulated in the coarsest [24]. Therefore, at least in part, the higher presence of trace elements in the fine fractions could be due to the greater amount of soil material or its finer fractions in the composts. This could be the case, particularly in the sewage compost, that the fine clay particles suspended in the wastewater constituted the mineral part of this compost, and also of the alperujo compost, where its management in agricultural land can incorporate soil into the vegetable material of the olive. The enrichment of the finest physical fractions in the MSW compost was likely due to the solubilization of the metals by the organic acids produced during the microbial decomposition of the organic matter. The leached metals then undergo adsorption onto the finer particles due to the fact of their larger surface area and higher ion exchange capacity [8].

Differences in the elemental concentrations of different granulometric fractions force the careful homogenization of a compost sample if it is to be analyzed directly by pXRF, without prior grinding. Without this homogenization, the results would be very dependent on the specific particles on which the incident RX beam was focused. In addition, an important and known fact for solid materials is that the intensity of the fluorescence radiation depends on the particle size, especially for light elements (F to Fe) [25].

3.4. Effect of the Sample Grinding on the Elemental Concentration Determined by pXRF

The elemental concentrations before and after grinding the whole compost samples are shown in Table 4. Upon grinding, significantly higher concentrations of the elements Rb, Zr, and P were recorded in the sewage compost, Sr and P in the MSW compost, and Al in the alperujo compost. The highest variation was 23.5% for the Sr concentration in the MSW compost. Actually, the elements Sr, Rb, and Zr are of little interest in the compost because they have no incidence at the level of plant nutrition or from an environmental point of view. The P concentration increased when the grinding was 15.2% in the MSW compost, and in the sewage compost, it was only 2.9% (percentages with respect to the value of the ground sample). On the contrary, the readings of Zn in the MSW and alperujo composts and Cu in the sewage and MSW composts decreased significantly. The reductions were 34% for the Cu concentration in the MSW compost and approximately 20% for the Zn concentration in both the MSW and alperujo composts. With the exception of the cases mentioned, the concentrations of most elements did not show significant differences and, in many cases, both of the values for each pair of the results were very similar. The reason that few differences were observed may be that the grinding process that was carried out had little effect on the finest particles, <0.5 mm, which represent an important weight fraction of the complete sample (57.5% and 29.0% in the case of the sewage compost and the MSW compost, respectively). This fraction was able to dilute the differences and mask possible grinding effects.

Table 4. Effect of sample grinding on the pXRF elemental readings in integral compost samples (comparison by *t*-test in three paired replicates).

Element	Compost	Whole Sample			Element	Compost			
		Unground	Sig. [1]	Ground			Unground	Sig. [1]	Ground
Rb	Sewage	30.6	*	32.3	$S \times 10^{-3}$	Sewage	20.1	ns	20.3
	MSW	16.2	ns	17.5		MSW	9.81	ns	9.13
	Alperujo	14.8	ns	14.5		Alperujo	3.85	ns	3.51
Zr	Sewage	99.0	*	114.6	$K \times 10^{-3}$	Sewage	10.4	ns	10.9
	MSW	45.8	ns	59.7		MSW	18.1	ns	18.3
	Alperujo	39.7	ns	35.9		Alperujo	45.3	ns	46.6
Sr	Sewage	155	ns	151	[2] $P \times 10^{-3}$	Sewage	13.9	*	14.3
	MSW	156	ns	204		MSW	5.95	**	7.02
	Alperujo	71.4	ns	68.9		Alperujo	1.99	ns	1.89
Zn	Sewage	464	ns	451	[2] $Si \times 10^{-3}$	Sewage	108	ns	112
	MSW	652	*	536		MSW	42.5	ns	46.1
	Alperujo	28.7	*	24.0		Alperujo	27.4	ns	31.8
Cu	Sewage	177	*	167	[2] $Cl \times 10^{-3}$	Sewage	ND		ND
	MSW	248	**	185		MSW	ND		ND
	Alperujo	71.2	ns	62.2		Alperujo	1.56	ns	1.55
Pb	Sewage	38.0	ns	37.1	[2] $Al \times 10^{-3}$	Sewage	14.9	ns	16.6
	MSW	81.2	ns	82.2		MSW	8.02	ns	7.58
	Alperujo	ND		ND		Alperujo	3.76	*	4.47
Mn	Sewage	376	ns	426	[2] $Fe \times 10^{-3}$	Sewage	51.6	ns	50.4
	MSW	140	ns	171		MSW	27.1	ns	26.3
	Alperujo	ND		ND		Alperujo	5.02	ns	4.92
As	Sewage	12.7	ns	12.2	[2] $Ca \times 10^{-3}$	Sewage	48.3	ns	48.7
	MSW	ND		ND		MSW	98.3	ns	100.3
	Alperujo	ND		ND		Alperujo	57.2	ns	58.0
V	Sewage	69.5	ns	79.3	[2] $Bal \times 10^{-3}$	Sewage	715	ns	704
	MSW	ND		ND		MSW	774	ns	774
	Alperujo	ND		ND		Alperujo	875	ns	871
Ti	Sewage	2478	ns	2498					
	MSW	1100	ns	1067					
	Alperujo	634	ns	764					

[1] ns: Non-significant difference. * $p < 0.05$; ** $p < 0.01$; [2] For these elements, measurements were conducted in the precalibrated mining mode; for the rest of the elements, the measurements were performed with the precalibrated soil method.

To overcome this equalizing effect of the finer particles, the same comparisons between ground and unground samples were carried out for the size fractions greater than 0.5 mm (that is, three paired replications for the 2–5 mm and three paired replications for the 0.5–2 mm). The statistical comparisons for these fractions are shown in Table 5. As can be seen, the number and the magnitude of the differences between some elemental concentrations in the ground and unground samples were more evident. In the ground samples, very significant higher readings were obtained for the major elements K, P, Si, and Al as well as for V and Ti. The variations were important, with the values in the ground samples reaching +46.7% of the Si concentration in the MSW compost. The reason for the high difference in the Si concentration could be related to the presence of glass particles in the urban waste. These particles, which were dense, could have settled below the surface layers when the XRF cups were prepared for scanning, leaving them out of range of the incident XR beam. In the sewage and alperujo composts, Si concentration increases close to +27% were also recorded with the grinding process. In the sewage compost, higher readings were obtained in the ground samples for the elements Al, Si, K, Ti, and V. In

the MSW compost, the results were higher in the ground fractions for the elements Si, P, and Pb. In addition, in the alperujo compost, differences were observed for the Si, K, and Ti concentrations.

Table 5. Effect of grinding the coarser than 0.5 mm particle size fractions on the pXRF elemental readings (comparison by *t*-test in the paired replicates per each fraction).

Compost	Element	Unground	Sig. [1]	Ground	Element	Compost	Unground	Sig. [1]	Ground
Rb	Sewage	26.0	ns	28.1	S × 10⁻³	Sewage	16.8	ns	17.4
	MSW	19.1	ns	18.0		MSW	8.14	ns	7.70
	Alperujo	13.8	ns	14.4		Alperujo	3.42	ns	3.21
Zr	Sewage	82.7	ns	95.1	K × 10⁻³	Sewage	7.84	**	10.63
	MSW	68.7	ns	75.4		MSW	15.7	ns	16.2
	Alperujo	34.3	ns	35.6		Alperujo	40.2	**	46.2
Sr	Sewage	159	ns	138	[2] P × 10⁻³	Sewage	12.5	ns	13.4
	MSW	157	ns	184		MSW	4.72	*	6.17
	Alperujo	66.2	ns	67.4		Alperujo	1.97	ns	1.80
Zn	Sewage	475	**	405	[2] Si × 10⁻³	Sewage	81.9	**	112
	MSW	677	**	480		MSW	36.2	**	67.9
	Alperujo	26.3	ns	24.8		Alperujo	21.6	**	29.5
Cu	Sewage	190	**	164	[2] Cl × 10⁻³	Sewage	ND		ND
	MSW	256	**	156		MSW	ND		ND
	Alperujo	72.9	ns	71.0		Alperujo	1.32	*	1.55
Pb	Sewage	35.3	ns	32.1	[2] Al × 10⁻³	Sewage	12.4	**	17.0
	MSW	52.9	*	63.0		MSW	6.77	ns	7.84
	Alperujo	ND		ND		Alperujo	3.33	**	4.73
Mn	Sewage	408	ns	391	[2] Fe × 10⁻³	Sewage	51.0	*	44.7
	MSW	132	ns	232		MSW	24.5	ns	24.6
	Alperujo	ND		ND		Alperujo	4.43	ns	4.81
As	Sewage	13.3	ns	12.5	[2] Ca × 10⁻³	Sewage	54.2	ns	50.3
	MSW	9.82	*	8.21		MSW	102	ns	109
	Alperujo	ND		ND		Alperujo	47.9	ns	52.3
V	Sewage	55.9	*	67.8	[2] Bal × 10⁻³	Sewage	745	**	715
	MSW	ND		ND		MSW	776	*	747
	Alperujo	ND		ND		Alperujo	895	ns	880
Ti	Sewage	1733	**	2404					
	MSW	957	ns	1148					
	Alperujo	537	**	765					

[1] ns: non-significant difference. * $p < 0.05$; ** $p < 0.01$; [2] For these elements, the measurements were conducted in the precalibrated mining mode; for the rest of the elements, the measurements were performed with the precalibrated soil method.

The attenuation of the X-rays within the individual coarse particles is known as the particle size effect. This effect is more pronounced for light elements (Z < 20), among which would be elements such as Al, Si, P, and K [26]. However, signal attenuation in coarse, unground particles was also observed in this study for other elements with Z > 20. The elements Ti, Sr, and Zr were more abundant in the soil, while they were found in reduced concentrations below 100 mg kg⁻¹ in the plant material [22,27]; therefore, the increases in the concentration readings found for them when grinding must be related to the mineral fraction of the composts before their organic fraction. Although the compost samples were homogenized before being placed in the measuring cup, it was possible for the fine and dense soil particles to settle in the porous medium constituted by the coarse particles of the plant material, thus escaping from the X-ray beam. In this way, possibly, the increases in

the reading when grinding were due to the superposition of both effects: the particle size effect and the lack of the homogeneity of the sample.

Contrary to the previous elements, the measured concentrations of Zn and, especially, Cu were lower in the milled fractions of the sewage and MSW composts, the As concentration decreased with grinding in the MSW compost, and the Fe concentration decreased in the sewage compost. Lower readings for Fe concentration were found in [28] when grinding soils to less than 0.15 mm.

In summary, higher readings were obtained for the concentrations of the elements Rb, Zr, Sr, Pb, V, Ti, K, P, Si, and Al and lower for Zn and Cu in the ground samples, although the type of compost determined in which elements in particular differences appeared and the magnitude of the difference.

These results are consistent with those of McWhirt et al. [10], who indicated that the influence of the particle size on the detectability is different for each element. However, these researchers found that Zn, K, Ca, and Cu showed little change between particle size classes but As and Ni detection was clearly influenced (the comparison here was between types of compost with particle sizes <5 and >5 mm).

An alternative explanation for the differences in the element concentrations among the ground and unground samples can be based on the different organic matter contents that the different granulometric fractions could eventually have. In a study with soil samples, Chen et al. [29] found a correlation between the results measured with pXRF and the organic matter content of the soil, among other factors. In Chen et al. [29], the inclusion of the organic matter content allowed for significant improvements in the regression models for the concentrations of Pb and Sr. The organic matter contents of the soils in this study were between 3.9 and 33.4 g kg^{-1}, values much lower than those of the compost samples in our study (310–726 g kg^{-1}, Table 1). Additionally, under this hypothesis, it would be expected that the alperujo compost, with a higher content of organic matter (Table 1), would have presented more differences in the concentrations between the ground and unground samples (Tables 4 and 5), which was not observed. In a previous study by our team [20], with varied compost samples with different organic matter content, the Bal parameter, which is related to the organic matter content of the samples, was only relevant in the predictive linear fits of the S and Ni contents, elements that in the present composts did not show variations due to grinding.

The differences depended on the type of compost, being very variable between them. In these circumstances, it was not possible to establish correction factors that allow for correcting the pXRF readings depending on whether the sample was ground.

Several of the elements that presented significant variations are relevant from the point of view of the environmental (Pb, Zn, and Cu) and agronomic compost quality (the plant nutrients K and P, among others), and their contents in compost are regulated (for example, in Europe by the regulation [19]). Thus, users must be aware that pXRF readings may present deviations depending on the granulometry of the sample and its nature, and it would be advisable to adopt standardized criteria regarding the grinding and homogenization of the products. Although for a screening analysis, the pretreatment of the sample may be of less relevance, as other authors have indicated [11], if quantitative results are required, pretreatment (i.e., drying, grinding, and homogenization) is necessary.

- Method of preparation affects pXRF data quality;
- Accuracy of pXRF data may be element specific [30].

4. Conclusions

The method of the compost pretreatment affects pXRF readings. Relevant elements, such as Cu, Zn, and P, as well as elements of little environmental interest, such as Rb, Zr, or Al, resulted in different concentration measurements in ground and unground compost samples. Other elements such as K, Si, or Ti or, to a lesser extent, Fe, Pb, or As were also variable with the grinding of the coarse granulometric fractions of the compost. Thus, the intensity of the effect depended on the element in question and the type of compost. As the

effect can be important for certain elements necessary to ensure the quality of the composts, if we want to obtain reliable quantitative elemental composition results, it is necessary to adopt standardized procedures for grinding and homogenizing the samples. In the future it will be necessary to investigate faster and simpler sample processing procedures compatible with the immediate character analysis performed with pXRF.

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