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Influence of chemical and mineralogical properties of organic amendments on the selection of an adequate analytical procedure for trace elements determination

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ABSTRACT

Six digestion procedures were tested to improve extraction methods for determination of trace elements in various organic amendments with high inorganic fractions. These procedures were tested in terms of pH, $CaCO_3$, organic matter, elemental analysis, BCR sequential extraction and X-ray diffraction analysis. Aqua regia extraction (ISO 11466), total digestion $HF–HNO_3–HClO_4$ and four microwave-assisted digestions (i.e., HNO_3, $HCl–HNO_3$, $HNO_3–HF$ and $HCl–HNO_3–HF$) were used. The effect of acid mixtures on microwave-assisted digestion of mineral fractions was assessed by Si and Al analysis and X-ray diffraction in the solid residues obtained. Microwave HF acid mixtures obtained highest trace element recoveries for all tested metals except Al. CaF_2 and $CaAlF_5$ precipitates were also detected using X-ray diffraction in the residues after microwave digestions with HF acid mixtures of amendments with high calcium content. A decision flowchart was suggested to determine the best acid mixture according to the amendment and the metals to be analyzed.

1. Introduction

Composted organic wastes are commonly used as organic amendment, fertilizer or growing media in agriculture and degraded soil recovery. The composts supply organic matter, nutrients and microorganisms, which improve the physico-chemical and microbiological soil properties and the fertility status. However, organic wastes can be an important source of trace elements in soils. During the stabilization process of organic matter and nitrogen, trace elements are concentrated in the compost matrix due to mass loss [1]. A major limitation of compost application to soil is thus the potential for high trace elements content.

The incorporation of trace elements after repeated applications of organic amendments in soils can have phytotoxic effects and also affect soil microorganisms [2]. In addition, once trace elements are applied, they have very long residence times in soil [3]. An exhaustive control of trace elements in agricultural soils is therefore necessary to prevent soil degradation and trace elements incorporation in the food chain. Fast, repeatable and robust methods for trace elements analysis are necessary to control organic amendments samples with different compositions and from multiple origins.

Regulations and guidelines for compost applications are currently based on total metal loadings. Traditionally, the literature and international directives have described compost as materials based in organic components, so analytical procedures to digest them and determine trace elements content are usually focused on the total oxidation of the organic matter. However, organic amendments can be composed of diverse organic wastes and inorganic materials including soils, sediments and inorganic residues, such as lime, gypsum, clay and silica.

The inorganic fraction may be relatively large in some organic amendments. In numerous countries, composted and co-composted wastes are being generated with appreciably high mineral fractions. For example, sewage sludge produced as a by-product of municipal wastewater treatment is composed of approximately 50% organic and 50% inorganic material [4]. Because the analysis of the trace elements concentrations in these waste materials is crucial for monitoring and risk assessment, the methods of sample mineralization must be able to liberate the trace elements associated with the inorganic fractions of compost.

In the literature, various methods for compost digestion have been described: dry ashing [5], heated mixture of acids [6], microwave-assisted wet digestion [7] and various acid mixtures

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Abbreviations: SMC, spent mushroom compost; GWS, green waste + sewage sludge compost; BP, black peat; HWC, horticultural waste compost; AR, $HCl–HNO_3$ acid mixture; ARF, $HCl–HNO_3–HF$ acid mixture; N, HNO_3 acid mixture; NF, $HNO_3–HF$ acid mixture; A, anorthite; Al, aluminum hydroxides; C, calcite; CF, CaF_2; D, dolomite; F, $AlCaF_5$; Fe, iron oxides; G, gypsum; H, hallosite; I, illite; K, kaolinite; M, mica; P, $AlPO_4$; Q, quartz; W, whewelite.

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for wet digestions (e.g., HNO_3–HCl [8–10], HNO_3–$HClO_4$ [11–13], HNO_3, [10,13,14], HNO_3–HF–H_2O [15], HNO_3–H_2O_2 [16], and HNO_3–HF–$HClO_4$ [13]). Not all acid mixtures completely attack the inorganic fraction, so hidrofluorhidric acid is sometimes necessary for complete digestion. Hseu [6] and Sandroni and Smith [14] reported that HNO_3 produced the best recoveries for metal analysis except Al, which required HF.

Microwave-assisted acid extraction has proven to be a suitable method for the digestion of complex matrices, such as soils, sediments, biosolids and compost [14,17–19]. This procedure presents great advantages over traditional wet digestion, such as reduced duration of digestion, smaller quantities of acids, improved detection limits, less frequent contamination and loss of volatile analytes and increased reproducibility and accuracy.

Sequential extraction procedures have been used to determine the chemical forms of trace elements present in sediments and soils, and also in organics amendments, such as green waste, biosolids and municipal solid waste composts [1,3,8,20,21]. Such information is traditionally considered to be valuable for predicting metal mobility, bioavailability and leaching rates when composts are applied to soils [22]. Information from sequential extraction can also be considered in the selection of the optimal method for the extraction of trace elements present in composts. However, metal fractionation using sequential extractions is largely operational because the reagents are not completely selective and re-adsorption and redistribution of metal ions after release can occur [23]. For this reason, better understanding of trace elements speciation in the amendments can be obtained by combining different analytical methods, such as basic characterization, sequential extraction and mineralogical analysis, to better understand the chemical forms of trace elements and the mineralogical composition of organic amendments for selecting the most adequate analytical procedures for trace elements determination.

The purposes of this work were as follows: (1) to evaluate the Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb content in four organic amendments with high inorganic fractions using different digestion methods. These methods included the conventional aqua regia extraction ISO 11466 [9], an open-vessel HF–HNO_3–$HClO_4$ total digestion, and four microwave-assisted methods (i.e., HNO_3 and HCl–HNO_3 as acid extractable and HNO_3–HF and HCl–HNO_3–HF as total digestion) and (2) to select the most appropriate microwave-assisted acid digestion method for trace elements in amendments according to their chemical and organic compositions, sequential extraction data and mineralogical changes in residues after microwave-assisted acid digestion.

2. Experimental

2.1. Samples and characterization

The following organic amendments were used: (1) Spent mushroom compost (SMC). Initial compost is produced from wheat straw (55%), grape marc (15%) and poultry litter (30%) (m/m); this is commonly used as a mushroom (*Agaricus bisporus*) cultivation medium. After cultivation, waste is composted for 3 months. (2) Green waste + sewage sludge (3:1, m/m) (GWS). This mix is composted in tunnels with forced air for 14 days and matured in the open air. Composting is completed in approximately 6 months. (3) Natural black peat (BP), obtained from northern Spain. (4) Horticultural waste compost (HWC), obtained from greenhouse production, sieved at <25 mm and composted in the open air for 90 days.

Accuracy of analysis was evaluated using a Certified Reference Material: sewage sludge LGC6181 from LGC Standards (UK). The extractable metal content refers to metals soluble in hot aqua regia using method based on ISO 11466 [9].

All samples were air-dried for 14 days, and electrical conductivity (EC) and pH were determined in water extracts (1:5, v/v) using a conductivity meter (Crison CM 2200, Barcelona, Spain) and a pH electrode (Orion 720A, Beverly, MA, USA), respectively. Organic matter content was determined by mass loss-on-ignition at 450 °C over 4 h. Dry samples were milled and sieved to 100 μm. $CaCO_3$ content was analyzed by calcimetry. Total carbon, nitrogen, hydrogen and sulfur were analyzed using combustion (LECO CHNS-932 analyzer, USA).

A mineralogical characterization of the raw amendments samples and their solid residues remaining after microwave-assisted digestion was carried out by X-ray diffraction (Panalytical X'Pert Pro, Almelo, The Netherlands). The configuration of this apparatus was $\theta/2\theta$ with an X'Celerator detector. Diffraction profiles were analyzed using X'Pert High Score Plus software and PDF-4 of the International Center for Diffraction Data for crystalline identification.

2.2. Reagents

All reagents used in sample digestion were better than analytical grade and supplied by Panreac (Spain), including Hiperpur HNO_3 (69%), Hiperpur HCl (35%), Hiperpur HF (48%) and Hiperpur $HClO_4$ (70%). Reagents used for sequential extraction were of analytical grade or better and supplied by Merck (Germany): acetic acid glacial, ammonium acetate, hydroxylammonium chloride, Suprapur hydrogen peroxide (30%). Ultrapure water was obtained from a Milli-Q water purification system (Millipore Corporation, Spain) and used throughout the work. All glassware and plasticware used were washed with 5% (v/v) nitric acid and rinsed with ultrapure water.

2.3. BCR sequential extraction procedure

The optimized BCR sequential extraction procedure [23] was applied to the organic amendment samples. This extraction procedure consists of three steps: Step 1 (exchangeable and weak acid soluble fractions) with acetic acid (0.11 M, 16 h). Step 2 (reducible fraction; Fe–Mn oxides), with hydroxylammonium chloride (0.5 M, pH 1.5, 16 h). Step 3 (oxidizable fraction; organic matter and sulfides) with H_2O_2 (8.8 M, 2 × 1 h, 85 °C) followed by extraction with 1.0 M ammonium acetate. Additionally, a fourth step was added to dissolve the final residue. The residual resistant fraction represented metals that were strongly associated with crystalline structures of minerals and which were unlikely to be released under conditions that are normally encountered in the environment. This residual fraction is typically extracted with aqua regia (ISO 11466), but HF–HNO_3–$HClO_4$ total digestion was performed in this work instead.

2.4. Aqua regia extraction (ISO 11466)

The aqua regia extraction was based on the ISO 11466 [9] procedure. Briefly, 3 g (±0.1 mg) of sample was placed in a 250 mL Pyrex digestion tube; 21 mL of 35% HCl and 7 mL of 69% HNO_3 were added, then the sample was covered with a watch glass and pre-digested at room temperature for 16 h. Subsequently, the suspension was digested for 2 h under reflux conditions. After cooling, the suspension was filtered through an ashless Whatman 42 filter, diluted to 50 mL with 0.5 M HNO_3, and stored in polyethylene bottles at 4 °C for analyses. Blanks were also treated using the same procedure.

2.5. Total digestion (HF–HNO_3–$HClO_4$)

For this method, 1 g (±0.1 mg) of sample was placed into a Teflon open vessel. A 10 mL volume of 48% HF was then added and

Table 1
Acid volumes (mL) used in microwave-assisted digestion procedures.

	HCl	HNO_3	HF
Mixture AR	9.00	3.00	–
Mixture ARF	8.25	2.75	1.00
Mixture N	–	12.00	–
Mixture NF	–	11.00	1.00

pre-digested at room temperature over 16 h. Next, the suspension was heated until dryness on a sand bath; 10 mL of 69% HNO_3 and 5 mL of 37% $HClO_4$ were then added and the reaction was heated until approximately 0.5 mL final volume remained. The final volume was then made up to 50 mL with 0.5 M HNO_3 and stored in polyethylene bottles at 4 °C for later analyses. Blank digestions were also performed using the same protocol.

2.6. Microwave-assisted acid digestion

A pressurized closed-vessel microwave system (CEM Mars X Press, USA) was used to digest the samples. Microwave polyfluoroacetylene (PFA)-teflon vessels were cleaned before each digestion using 12 mL of 69% HNO_3, heated for 20 min at 200 °C and then rinsing with ultrapure water. After the microwave-assisted digestion procedure was optimized, the following conditions were employed: samples were accurately weighed to 250 mg (±0.1 mg) in microwave vessels. They were then subjected to four different digestion procedures using various acid combinations (Table 1) using the same solid sample/reagent volume ratio (250 mg to 12 mL). The digestion program consisted of a 15-min gradual increase to 200 °C, a 15-min digestion step at 200 °C and 1200 W and then a cooling stage. Acid mixtures used were selected according to previous reports for soil and compost trace elements analysis [10,13,18,24,25]. Blanks were processed in a method identical to the samples.

2.7. Trace and major elements analysis

Analyses were conducted on a ICP-MS spectrometer (Perkin Elmer Sciex Elan 6000) equipped with an autosampler (AS 91, Canada). The isotopes used for metals analyses were ^{52}Cr, ^{55}Mn, ^{56}Fe, ^{58}Ni, ^{63}Cu, ^{64}Zn, ^{114}Cd and ^{208}Pb. In addition, Al and Si (isotopes measured ^{27}Al and ^{28}Si) were analyzed for monitoring microwave-assisted digestion of silicates and aluminosilicates. Limits of quantitation were calculated over 10 measurements of the chemical blank from each acid mixture of microwave-assisted digestion as $10\sigma/b$, where σ is signal standard deviation and b is linear coefficient of the calibration graph.

2.8. Statistical analysis and chemical speciation software

SPSS 15.0 software was used for statistical analysis. Significant differences between different microwave-assisted acid digestions, aqua regia extraction (ISO 11466) and $HF–HNO_3–HClO_4$ total digestion were compared using 1-way ANOVA with Tukey's post-hoc test. Statistical significance was defined as $p < 0.05$. The V MINTEQ v.3.0 software was used to confirm Ca chemical species in microwave HF acid mixtures.

3. Results and discussion

3.1. Basic characterization of organic amendments

After a first approach based on basic chemical properties (Table 2), the selected organic amendments could be classified into three types:

1) SMC and HWC are composted agricultural wastes with high $CaCO_3$ and EC (10.4 and 11.6 dS m^{-1}), very low organic matter and C content (close to threshold values for organic amendments, as required by Spanish law RD 824/2005 [26]), and C/N values of approximately 10. These two materials have similar percentages of S.
2) GWS and LGC1681 present sewage sludge in their composition. They have remarkably high organic matter (50–60%), with almost 25% of their content coming from C. They also have several interesting similarities in pH, lack of carbonates and high EC. An important difference between these materials is elemental composition, as sewage sludge LGC6181 has higher values for N (low C/N) and S.
3) Natural black peat (BP), which has a lower pH value (4.86) and a low EC, but the highest organic matter (81%), C content and C/N.

3.2. Mineralogical characterization

All organic amendments were found to have quartz as the main mineral through X-ray diffractometry (Fig. 1). In addition to quartz, SMC showed calcite and gypsum. HWC showed calcite, dolomite, mica, anorthite and whewellite ($CaC_2O_4{\cdot}H_2O$) as secondary minerals. Whewellite also appeared in GWS, as did mica and anorthite. The presence of whewellite in HWC and GWS indicated the vegetal origin of these composts, as many plants contain calcium oxalate phytolites in their leaves, bark and wood as monoclinic whewellite crystals [27].

The secondary mineralogical composition of the reference standard material LGC1681 was gypsum, aluminum hydroxides and iron oxide. This was not surprising, as gypsum has been reported to precipitate during wastewater and sludge treatment [28]. In contrast, BP showed mica as a secondary mineral. Poorly crystalline iron hydroxides, such a ferrihydrite, might also have been present in SMC and BP due to the presence of a weak and broad XRD peak at 2.58 Å, but this was difficult to identify in bulk XRD analysis.

3.3. Distribution of trace elements in organic amendments according to the BCR procedure

The BCR extraction results are shown in Fig. 2. As can be seen, Cr, Fe, Ni and Pb were mainly associated with the residual fraction, suggesting that these metals were primarily contained in silicates and other resistant minerals. Other works obtained similar results

Table 2
Basic chemical characteristics and elemental analysis of organic amendments.

	pH	$CaCO_3$ (%)	EC[a] (dS m^{-1})	OM[b] (%)	C (%)	N (%)	H (%)	S (%)	C/N
SMC	7.02	28.1	10.4	25.2	12.4	1.37	1.73	0.21	10.7
GWS	7.19	–	2.00	58.1	26.2	1.41	3.49	0.04	23.9
BP	4.86	–	0.6	80.8	37.5	0.87	4.68	0.06	53.9
HWC	9.00	18.1	11.6	32.6	19.2	1.82	2.47	0.17	10.4
LGC1681	6.57	–	6.0	53.0	24.6	3.54	4.14	1.08	8.7

[a] Electrical conductivity.
[b] Organic matter.

for sewage sludge [20], municipal solid waste compost [21], and deinking paper fiber and green waste compost [1]. A particularity of LGC6181, and sewage sludge in general, was the great mobility of Ni compared to other trace elements [1,3,20]. The majority of Fe in the amendments was associated with the residual fraction (26–84%), followed by the oxidizable fraction (9–47%). This observation implied that Fe occurred in silicates and organic matter as sulfides with very little in the poorly crystalline hydroxides. Alonso et al. [20] found similar distribution patterns of Fe in sewage sludges.

Mn appeared in all four fractions with no preference for any particular one. In addition, most of the Cu was released by H_2O_2 extraction (70–85%), implying a great tendency to be bound in the organic fraction. Furthermore, a significant proportion of Cu (approximately 25%) was present in the residual fraction, suggesting a presence in resistant minerals. The majority of Cd was released during hydroxylamine–HCl extraction (17–71%), suggesting that Cd was primarily contained in reducible hydroxides and oxides. Very little Cd was present in the residual fraction (2–10%), except for HWC (24%). Finally, Zn was mainly associated with the reducible fraction (47–50%), except amendments with high $CaCO_3$ contents, and the organic fraction (26–74%); its residual fraction was variable from 4 to 56%.

The results from the sequential extraction procedure indicated that HF would be recommended for total digestion together with a strong oxidant acid in order to completely dissolve the organic and residual fractions of the amendments of interest.

3.4. Comparison of open system digestions

Table 3 shows the results of aqua regia extraction (ISO 11466) and total digestion ($HF–HNO_3–HClO_4$) of organic amendments. The precision of the methods was assessed by the percentage relative standard deviation (%RSD). For both methods, %RSD was good, generally <10% for all the metals and amendments. Pseudo-total digestion according to ISO 11466 obtained equal or higher concentrations of Cr, Mn, Ni, Cu, Zn, Pb and Cd (except for SMC) than total digestion. Only Fe concentrations were higher in the extracts from tri-acid total digestion for all amendments, suggesting the release of Fe included in the aluminosilicate phase during this treatment. These results indicated that open total digestion $HF–HNO_3–HClO_4$ produced losses specially Ni, Cu and Zn; similar results were obtained by other authors [24,29], suggesting the use of closed digestion methods.

3.5. Accuracy of open system digestions

The accuracy of the aqua regia extraction (pseudo-total digestion) and tri-acid total digestion was assessed with the analysis of the certified reference material LGC6181 which certified

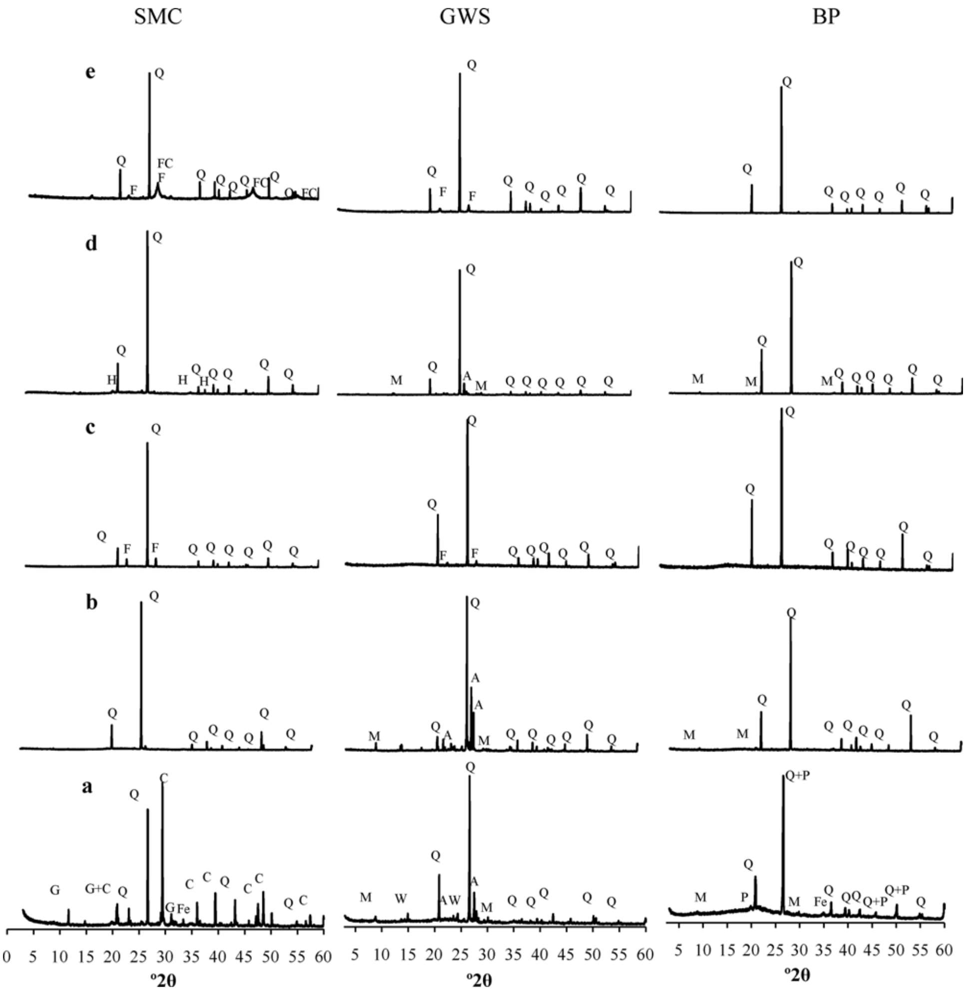

Fig. 1. X-ray diffractograms of SMC, GWS and BP (a) and their residues after four different acid mixture microwave-assisted digestion methods (b: AR; c: ARF; d: N; e: NF). A, anorthite; Al, aluminum hydroxides; C, calcite; CF, CaF_2; D, dolomite; F, $AlCaF_5$; Fe, iron oxides; G, gypsum; H, hallosite; I, illite; K, kaolinite; M, mica; P, $AlPO_4$; Q, quartz; W, whewelite.

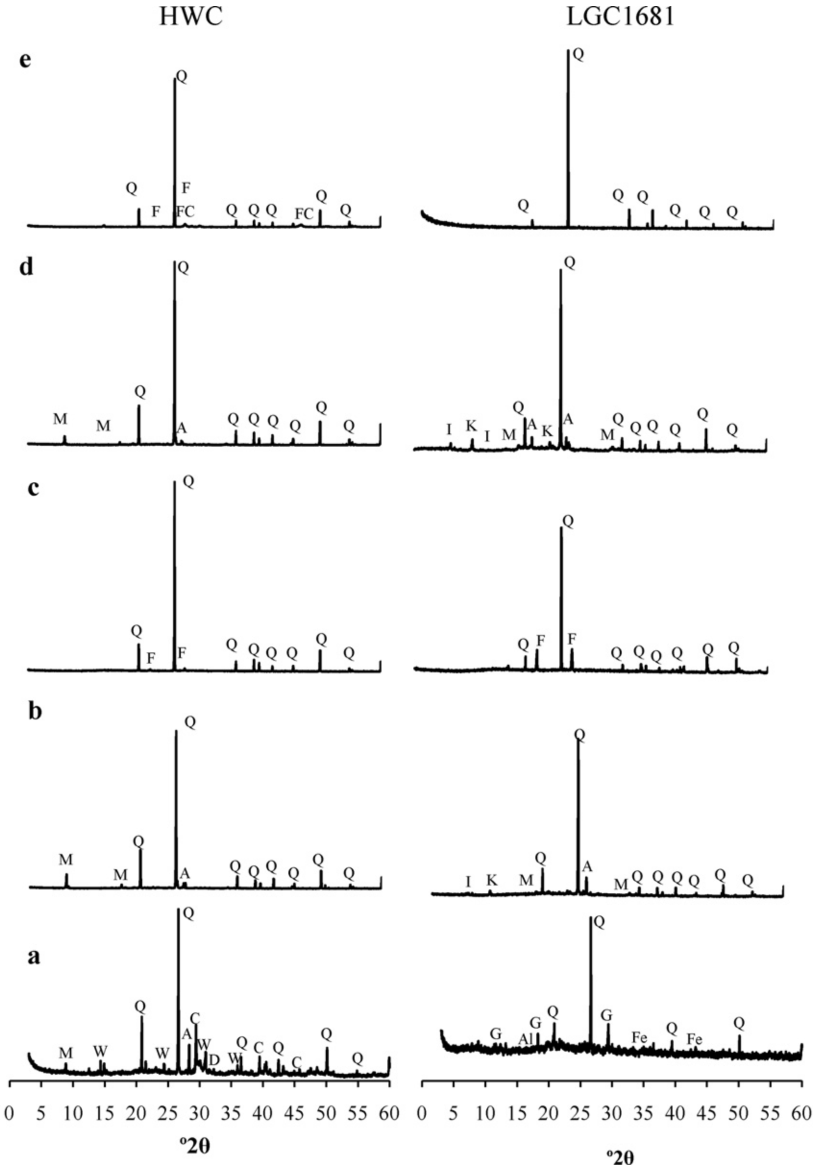

Fig. 1. (*Continued*).

values corresponding to the extractable metal contents (Table 4). The recovery of each metal was calculated based on the mean value of CRM LGC6181 [(measured concentration (mg kg^{-1})/mean certified value (mg kg^{-1})) × 100]. The accuracy was better for the aqua regia extraction (recovery ranged from 97% to 107%) compared to total digestion (recovery ranged from 39% to 101%). For both methods precision was very satisfactory, with %RSD < 5%. According to the ERM [30] aqua regia extraction using protocol ISO 11466 produces results that agree perfectly with certified values. However, HF–HNO$_3$–HClO$_4$ total digestion results only agreed for Cr and Mn.

Table 3

Multi-elemental analysis of four organic amendments using aqua regia extraction (ISO 11466) and HF–HNO$_3$–HClO$_4$ total digestion. Results are expressed in mg kg^{-1}. Letters indicate significant differences between digestion methods for each material and metal. RSD is given in brackets; $n = 3$.

	SMC		GWS		BP		HWC	
	Aqua Regia	HF–HNO$_3$–HClO$_4$	Aqua Regia	HF–HNO$_3$–HClO$_4$	Aqua Regia	HF–HNO$_3$–HClO$_4$	Aqua Regia	HF–HNO$_3$–HClO$_4$
Cr	83.0 (5)	86.6 (1)	355 (5)	383 (2)	99.8^{a} (1)	87.0^{b} (0.1)	322 (0.1)	324 (3)
Mn	318^{a} (6)	268^{b} (1)	237 (2)	225 (3)	22.2^{a} (2)	19.0^{b} (7)	372^{a} (1)	319^{b} (4)
Fe	8848^{b} (6)	11496^{a} (12)	8014^{b} (4)	9737^{a} (3)	2493^{b} (2)	3507^{a} (1)	9098^{b} (1)	11795^{a} (4)
Ni	36.5^{a} (6)	28.4^{b} (2)	130^{a} (4)	104^{b} (3)	29.5 (1)	28.3 (2)	122^{a} (2)	83.0^{b} (4)
Cu	30.1^{a} (7)	20.5^{b} (1)	94.4^{a} (4)	79.0^{b} (10)	3.96 (6)	3.55 (12)	153^{a} (2)	100^{b} (3)
Zn	139^{a} (6)	79.0^{b} (1)	120^{a} (5)	80.7^{b} (3)	45.5^{a} (23)	9.26^{b} (4)	248^{a} (2)	123^{b} (4)
Cd	0.144^{b} (5)	0.162^{a} (1)	0.273 (2)	0.263 (4)	0.147 (1)	0.140 (1)	0.453^{a} (7)	0.397^{b} (3)
Pb	10.1^{a} (3)	5.42^{b} (6)	20.2 (4)	21.4 (4)	6.13 (4)	6.11 (14)	21.0 (2)	20.5 (4)

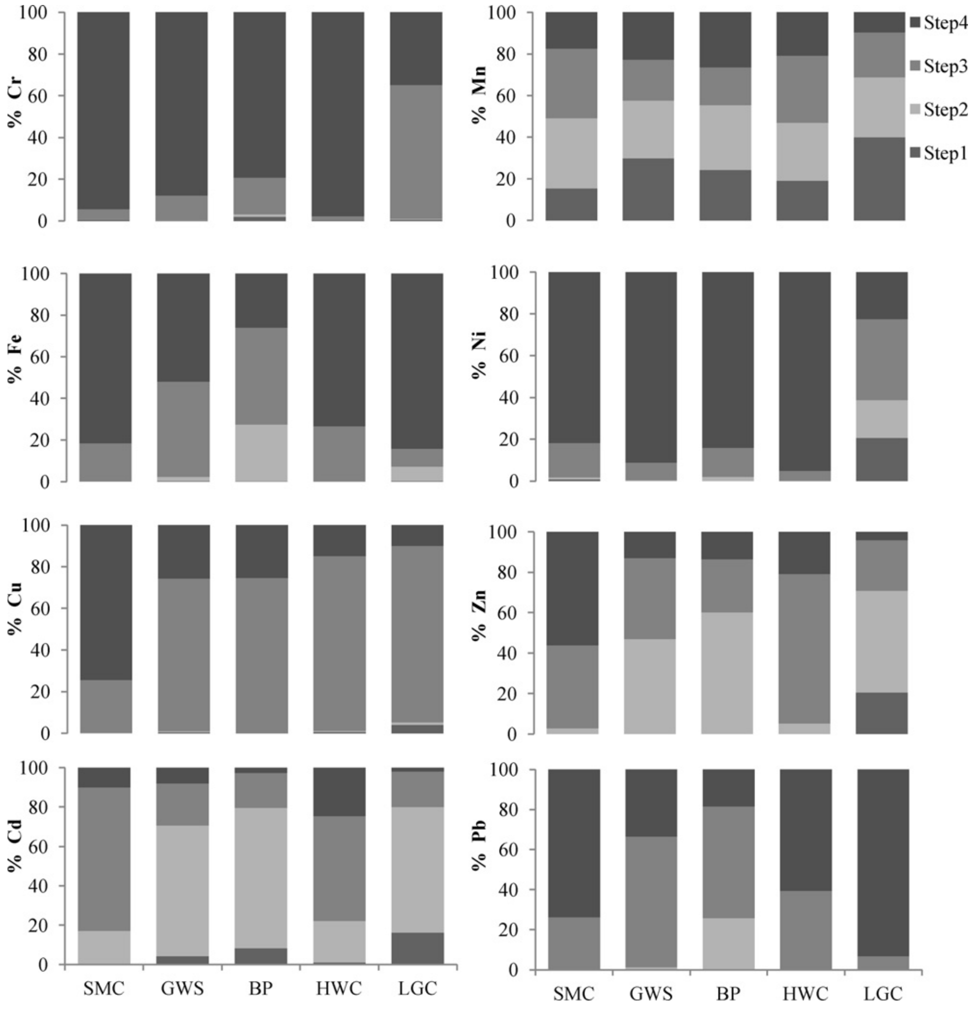

Fig. 2. Distribution of fractions for BCR sequential extraction of Cr, Mn, Fe, Ni, Cu, Zn, Cd and Pb of organic amendments. Step 1 is exchangeable, water and acid soluble fraction, Step 2 is reducible fraction, Step 3 is oxidizable fraction and Step 4 is residual fraction. Results are mean percentages for $n = 3$.

Due to these results, only the aqua regia extraction using ISO 11466 is considered adequate for multi-elemental analysis for this kind of organic amendments.

For further comparisons, concentrations of trace elements of amendments obtained with aqua regia extraction using ISO11466 are considered as 100% recovery.

3.6. Quality control of microwave-assisted closed vessel digestions

The quality control of the microwave-assisted acid digestions was performed by comparison with the LGC6181 (Fig. 3). Reproducibility of four acid mixtures was very good with %RSD in most cases lower than 5%. However, recovery for the microwave-assisted AR procedure was lower than aqua regia extraction (ISO 11466) for all the metals with respect to certified values. Additionally, microwave-assisted N digestion led to similar results of those for LGC6181 with the exception of Zn. Nitric acid microwave-assisted digestion has been considered an alternative for aqua regia extraction for samples with high organic matter content [13].

Total digestion procedures using HF (ARF and NF) showed higher concentrations than AR and N for all trace elements and major recoveries up to100% for Cr, Mn, Fe and Pb, between 111 and 123% (Fig. 3). These results could be attributed to more complete

Table 4
Multi-elemental analysis of Certified Reference Material LGC6181 using aqua regia extraction (ISO 11466) and $HF–HNO_3–HClO_4$ total digestion. Results are expressed as recovery percentage (Rec) of certified values and relative standard deviation (RSD). Letters indicate significant differences between digestion methods for each metal; $n = 3$.

	LGC6181	Aqua regia		$HF–HNO_3–HClO_4$	
	Certified (mg kg^{-1})	Rec (%)	RSD (%)	Rec (%)	RSD (%)
Cr	78 ± 8	105^a	0.4	96^b	1
Mn	454 ± 23	102	2	101	3
Fe	40300 ± 2300	100^a	1	88^b	3
Ni	45 ± 3	107^a	2	81^b	1
Cu	354 ± 18	100^a	2	71^b	2
Zn	1100 ± 50	102^a	2	92^b	4
Cd	5.8 ± 0.3	103^a	2	78^b	2
Pb	105 ± 8	97^a	3	39^b	10

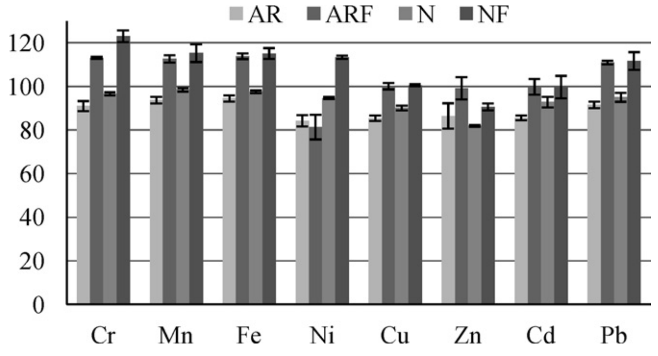

Fig. 3. Trace elements microwave-assisted acid digestion recoveries (%) of four acid mixtures (AR, ARF, N, NF) obtained from LGC1681. Bars indicate standard deviation; $n = 3$.

digestion of silicate components present in the sewage sludge LGC6181. These higher recoveries meant that ISO 11466 (extractable aqua regia metals) did not completely digest the test material, so the acid mixtures ARF and NF were more effective in sewage sludge matrix digestion and therefore in metal extraction strongly associated with mineral matter.

Limits of quantitation (LOQ) of microwave-assisted acid digestions (Table 5) were significantly lower than those obtained in the literature for determining and monitoring trace elements of organic amendments [31]. Especially remarkable were the low LOQ values for Cd (0.002–0.006 mg kg^{-1}). The use of HF in general increased LOQ, only Cd in ARF mixture and Ni and Zn in NF mixture got LOQ lower. For pseudo-total digestions, AR mixture produced LOQ major than N except Cu and Zn. For total digestion ARF mixture produced major LOQ except Mn. As general pattern, the mixture of acids produced an increase of LOQ values.

3.7. *Effects of microwave-assisted acid mixture digestions on the inorganic matrix of amendments*

Visual observation of the solid residues remaining following the four microwave-assisted acid digestions showed remarkable differences. HF acid mixture digestion on amendments with high $CaCO_3$ contents (SMC, HWC) created a white precipitate, which was more abundant in SMC. Samples characterized by the absence of $CaCO_3$ content (BP, GWS, LGC6181) digested with HF acid mixtures showed a minor quantity of solid residue. In these amendments, the acid mixture NF looked to be most effective because very little residue remained after microwave-assisted digestion.

X-ray diffractograms of organic amendments and their residues after the four microwave-assisted acid mixtures digestions are shown in Fig. 1. In general, similar patterns were observed in the mineralogical composition of the samples after the digestion procedures. Interestingly, all residues after all microwave-assisted acid digestions showed residual quartz. In addition, calcite, dolomite, gypsum, whewellite, Al hydroxides and Fe oxides were attacked by the four acid mixtures assayed and not detected in the residues. Acid mixtures, ARF and NF, completely digested silicate compounds, such as mica, ilite, kaolinite and anorthite.

Table 5
Limits of quantitation (LOQ, mg kg^{-1}) of acid mixtures after ICP-MS analysis.

	AR	ARF	N	NF
Al	2	5	1	3
Si	179	188	128	147
Cr	0.2	0.2	0.03	0.03
Mn	0.03	0.06	0.01	0.08
Fe	9	9	3	7
Ni	0.2	0.3	0.1	0.07
Cu	0.08	0.1	0.08	0.07
Zn	0.5	0.8	0.8	0.3
Cd	0.006	0.004	0.002	0.002
Pb	0.04	0.06	0.02	0.02

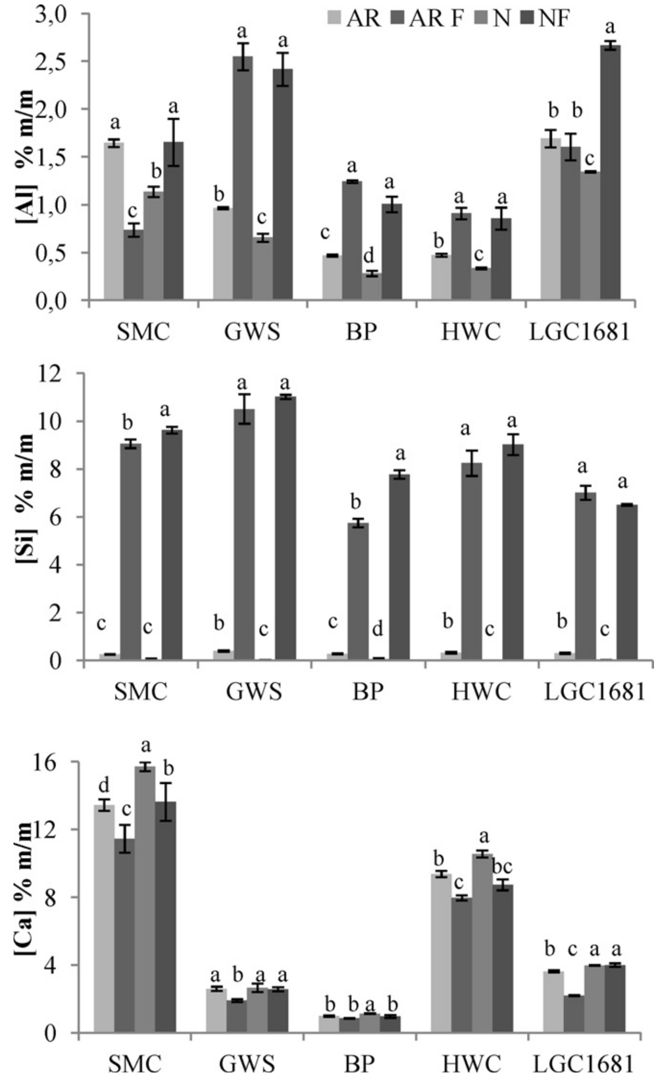

Fig. 4. Concentrations of Al, Si and Ca from four acid mixture microwave-assisted digestions (AR, ARF, N, NF). Bars indicate standard derivation ($n = 3$), and different letters indicate significant differences at $p < 0.05$.

XRD patterns of the residues, except those obtained in BP, after ARF and NF microwave-assisted digestion (Fig. 1c and e, respectively) showed three peaks at 3.15, 3.93 and 1.82 Å for $CaAlF_5$, with different intensities for each material. This result suggested the formation of calcium fluoroaluminate during both ARF and NF digestions. These reflections were more intense for SMC and LGC6181, and a significant decrease in recoveries of Al (56 and 40% respectively) and Ca (18 and 45%) employing ARF vs NF was also observed. These results suggested an important $CaAlF_5$ formation stage probably due to the high Ca and Al content of these materials (Fig. 4). However, $AlCaF_5$ was not detected for BP residues due to the low content of Ca and Al. In support of these observations, Marin et al. [18] reported Ca–F and Al–F complexes in calcareous soils after microwave-assisted HF digestion.

Additional broad peaks occurred at 1.93, 3.15 and 1.65 Å in the samples with high $CaCO_3$ content (SMC and HWC) only after NF microwave-assisted digestion. These reflections corresponded to CaF_2 and their intensities were higher in SMC than HWC, in agreement with the higher SMC Ca content (Fig. 4). The lack of CaF_2

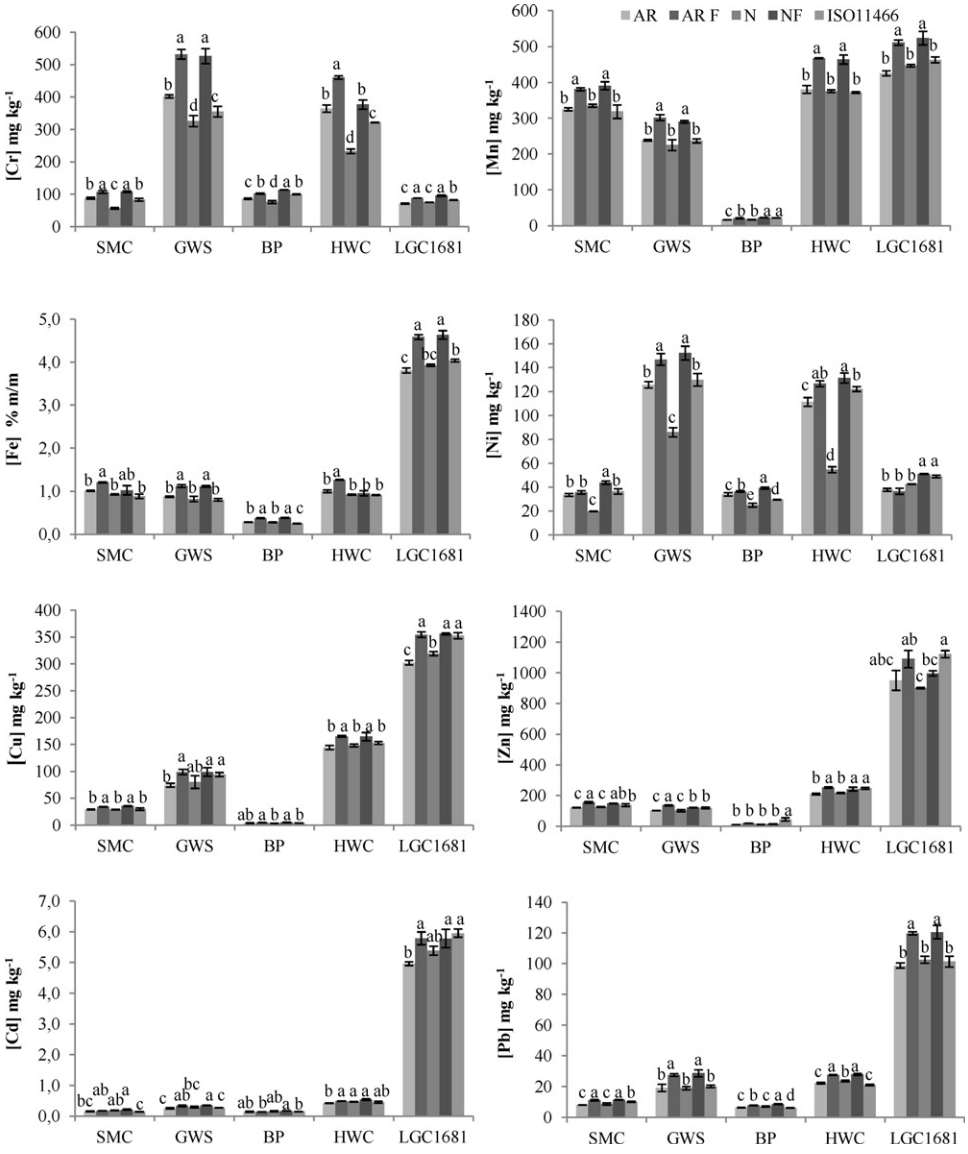

Fig. 5. Comparison of trace elements concentrations of four acid mixture microwave-assisted digestions (AR, ARF, N, NF) and ISO 11466. Bars indicate standard derivation ($n = 3$), and different letters indicate significant differences at $p < 0.05$.

in the solid residue after ARF digestion could suggest inhibition of formation by HCl. This hypothesis was confirmed by chemical speciation models performed in Visual Minteq 3.0. This model revealed that $CaCl^{+}_{(aq)}$ was the predominant Ca species under ARF digestion conditions.

Decomposition of aluminosilicates in each microwave-assisted acid mixture digestion was determined through the aluminum and silicon concentrations (Fig. 4). As can be seen, microwave ARF and NF digestions liberated higher concentrations of Al and Si than AR and N. Similar results were obtained by Sandroni and Smith [14] for Al in sewage sludge when employing HF. However, aluminum concentrations of SMC decreased with ARF and did not increase with NF, while Al concentrations of LGC6181 with ARF did not increase due to the formation of $CaAlF_5$. Furthermore, microwave-assisted AR digestion liberated higher Si and Al concentrations than microwave-assisted N digestion, because hot aqua regia is capable of dissolving tri-octahedral clays, primary and secondary salts and hydroxy oxides of amorphous aluminosilicates [32]. Silicon

Table 6
Linear correlation coefficients (r) between trace elements content of the residual fraction of BCR sequential extraction and metal concentration increase when HF was employed ($n = 15$).

	Cr	Mn	Fe	Ni	Cu	Zn	Cd	Pb
ARF-AR[a]	0.935***	0.827***	0.954***	0.917***	0.816***	0.529*	0.629*	0.916***
NF-N[b]	0.911***	0.850***	0.844***	0.974***	0.749***	0.565*	0.638*	0.798***

[a] Increase of metal concentration using acid mixtures ARF vs AR.
[b] Increase of metal concentration using acid mixtures NF vs N.
* $p < 0.05$.
** $p < 0.01$.
*** $p < 0.001$.

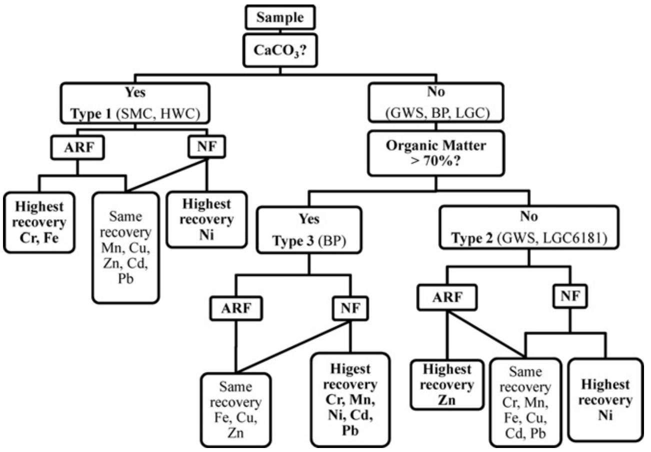

Fig. 6. Decision flowchart for the selection of a total digestion method for organic amendments according to chemical characteristics.

concentrations obtained with HNO_3 microwave extraction digestions were smaller than the quantitation limit except for black peat.

3.8. Comparison of microwave-assisted digestion of organic amendments

Microwave acid mixture digestion procedures were compared to each other and with the ISO11466 method that was previously checked in Section 3.5. Results are shown in Fig. 5.

Microwave-assisted AR and N digestions liberated similar concentrations of trace elements to ISO11466, except for Cr and Ni, which were extracted mainly in the residual fraction during the BCR procedure. For these metals, microwave-assisted AR digestion released significantly larger amounts than microwave-assisted N digestion. Florian et al. [7] reported similar behavior for microwave nitric acid and HCl:HNO_3 (3:1) digestions with respect to Ni and Cr.

Acid mixtures ARF and NF (with HF) more efficiently attacked aluminosilicates of samples, as is shown by the lack of aluminosilicate compounds in the XRD of residues after microwave-assisted HF digestions (Fig. 1) and higher Si recoveries (Fig. 4). Therefore, microwave-assisted HF digestions were more efficient and obtained higher trace elements concentrations than AR, N and ISO11466.

The increase in recoveries obtained when HF was used had a positive correlation with trace elements extracted in the fourth step of BCR (Table 6). This correlation indicated that metals extracted with HF were absorbed into aluminosilicate compounds, while AR and N were not able to extract them. Consequently, HF must be included for total acid digestion of organic amendments with high inorganic fractions. However, underestimation of certain element concentrations has been reported due to their trapping in Ca–F and Al–F complexes in calcareous soils after microwave-assisted HF digestion [18]. For comparison, our results showed a significant decrease in Fe concentrations when CaF_2 was formed after NF microwave-assisted digestion of amendments (SMC and HWC) rich in carbonates. In addition, Zn showed lower recoveries in GWS and LGC6181 with NF than ARF. However, ARF microwave digestions had lower Ni recoveries for all materials tested. These results suggested a co-precipitation phenomenon for CaF_2 and $CaAlF_5$ detected by XRD analysis.

Fig. 6 summarizes the results obtained from the different microwave-assisted digestion procedures. This flowchart is proposed as a procedure decision tree for organic amendment digestion for trace elements analysis.

In the literature, there are few reference materials other than sewage sludge to be consulted for the validation of digestion methods for compost or organic amendments. The different behavior of organic amendments shown in this paper indicates that Certified Reference Materials other than sewage sludge are necessary for future method development.

4. Conclusion

Microwave-assisted HF acid mixtures were more effective in attacking the aluminosilicate fraction and increased trace elements and iron recoveries. Additionally, this study demonstrated the formation of precipitates in the residues of organic amendments rich in calcium minerals after microwave-assisted digestion with HF mixtures (i.e., $CaAlF_5$ formation after microwave ARF and NF digestion, and CaF_2 formation only after microwave NF digestion).

As was noted in the text, Al, Fe, Zn and Ni could be underestimated by microwave-assisted HF acid mixture digestion in amendments with high Ca content as a consequence of their trapping in calcium fluoroaluminates or calcium fluoride precipitates.

Based on the analytical results and the required time of extraction, microwave-assisted digestion with a mixture of 11 mL of HNO_3 (69%) and 1 mL of HF (48%) is recommended for complete digestion of organic amendments, while a mixture of 9 mL of HCl (37%) and 3 mL of HNO_3 (69%) is proposed for pseudo-total digestion.

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