

Comparison of Three Aqua Regia Digestion Methods for Twenty Florida Soils

Ming Chen* and Lena Q. Ma

ABSTRACT

It is important to evaluate different digestion methods to accurately determine elemental concentrations in soils. Three commonly used digestion procedures, hotplate aqua regia, microwave aqua regia, and microwave aqua regia + HF, were compared for digestion of three standard reference materials (SRMs 2704, 2709, and 2711) and 20 Florida soils (three groups of Quartzipsammements, one group of Alaquods, and one group of Paleodults). Sixteen elements (Al, Ba, Ca, Fe, K, Mg, Mn, P, Zn, As, Cd, Cr, Cu, Ni, Pb, and Se) were analyzed using either an inductively coupled plasma optical emission spectrometer (ICP-OES) or a graphite furnace atomic absorption spectrophotometer (GFAAS). Precise analysis was achieved for all elements except As (1.0–25%), Cd (1.8–22%), and Se (4.1–22%) in the SRMs using all three procedures, with the microwave aqua regia + HF procedure having slightly better precision (3.7%) averaged across all elements. Compared with the elemental recoveries in SRMs by the microwave aqua regia digestion (80%), microwave aqua regia + HF digestion achieved greater accuracy (94%), whereas the hotplate aqua regia digestion achieved less accuracy (74%). In general, the microwave aqua regia + HF digestion was overall the best procedure for determining concentrations of most metals in SRMs and Florida soils, followed by the microwave aqua regia and the hotplate aqua regia digestion. However, this so-called total–total digestion procedure (microwave aqua regia + HF) may underestimate total Pb concentration in Florida soils and total Al, Ca, Fe, Mg, and Ba concentrations in the Florida Paleodults.

ACCURATE DETERMINATION of potentially toxic trace metals in soils is important for cleaning up contaminated soils and monitoring land application of metal-bearing nonhazardous materials (Chen and Ma, 1998; Chen et al., 1999). Sample digestion is often a necessary step before determining metal concentrations in soils. The aqua regia (3:1, v/v, HCl to HNO₃) digestion procedure (ISO standard 11466) is considered adequate for analyzing total-recoverable heavy metals in soils of certain regions and is used to estimate the maximum element availability to plants (Vercoutere et al., 1995). Residual elements that are not released by aqua regia digestion are mostly bound to silicate minerals and are considered unimportant for estimating the mobility and behavior of the elements (Niskavaara et al., 1997).

The conventional aqua regia digestion procedure consists of digesting soil samples on a hotplate with a 3:1 mixture of HCl and HNO₃ (Nieuwenhuize et al., 1991). The nitric acid reacts with concentrated HCl to form aqua regia: $3\text{HCl} + \text{HNO}_3 \rightarrow 2\text{H}_2\text{O} + \text{NOCl} + \text{Cl}_2$. This digestion procedure is so widely used that the European Community Bureau of Reference has certified several

soil and sludge samples based on it, in addition to the total elemental concentrations (Vercoutere et al., 1995; Quevauviller et al., 1993). In many countries (excluding the USA), this procedure is required by regulations to estimate the impact of soil amendments such as sewage sludge on the environment (Krause et al., 1995; Marr et al., 1995; Vercoutere et al., 1995). However, this procedure is very tedious and time-consuming (Siaka et al., 1998). In addition, if open systems are used during digestion, there are risks of atmospheric contamination and volatilization losses of volatile compounds during the oxidation of organic substances of the soils (Kubrakova, 1997; Nieuwenhuize et al., 1991; Quevauviller et al., 1993).

Since the 1980s, microwave-assisted sample digestion techniques have become popular and are widely used (Chen and Ma, 1998; Quevauviller et al., 1993; Smith and Arsenault, 1996). Microwave-assisted aqua regia digestion using a Teflon bomb is considered a rapid sample digestion method (Marr et al., 1995; Nieuwenhuize et al., 1991; Paudyn and Smith, 1992; Rantala and Loring, 1989). This technique provides a rapid, safe, and efficient digestion and is not susceptible to losses of volatile metals. However, the aqua regia digestion failed to accurately quantify more than 20 elements in some sediments (Krause et al., 1995), especially K and Al, which are part of some clay mineral structures. Berrow and Stein (1983) reported that aqua regia extracted <70% of Cd, Mn, and Ni from some sediments. Recovery of 43 to 77% for Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, and Zn from AGAL-11 reference sediment was also reported by Siaka et al. (1998). Paudyn and Smith (1992) found that the typical elemental recovery in ashes and sediments using aqua regia digestion was ≈80%, though the recovery was higher for many elements (e.g., Al, Fe, Mg) using microwave rather than hotplate digestion.

Nadkarni (1984) reported that a mixture of aqua regia, HF, and H₃BO₃ provides satisfactory precision and accuracy for dissolving silica matrices. The following reactions occur during digestion: $6\text{HF} + \text{SiO}_2 \rightarrow \text{H}_2\text{SiF}_6 + 2\text{H}_2\text{O}$ (Wu et al., 1996) and $\text{H}_3\text{BO}_3 + 3\text{HF} \rightarrow \text{HBF}_3\text{OH} + 2\text{H}_2\text{O}$, and $\text{HBF}_3\text{OH} + \text{HF} \rightarrow \text{HBF}_4 + \text{H}_2\text{O}$ (Ryss, 1956). Adding boric acid in the second stage of the digestion not only complexes the free fluoride ions in the solution, but also facilitates the dissolution of the precipitated fluorides (Wu et al., 1996). However, when ICP-OES is used for analysis, adding boric acid can create a matrix effect and was reported to result in a 20% decrease in sensitivity for Mo, Ni, Pb, Sb, Se, and Sn, and a 50% and 70% decrease in sensitivity for P and S, respectively

M. Chen, Institute of Geography and Natural Resources, Chinese Academy of Sciences, Beijing 100101, China; L.Q. Ma, Soil and Water Science Dep., Univ. of Florida, Gainesville, FL 32611-0290. Approved for publication as Florida Agricultural Experiment Station Journal Series no. R-06802. Received 14 Sept. 1999. *Corresponding author (mchen@gnv.ifas.ufl.edu).

Abbreviations: DDW, deionized, distilled water; GFAAS, graphite furnace atomic absorption spectrophotometer; ICP-OES, inductively coupled plasma optical emission spectrometer; NIST, National Institute of Standards and Technology; RSD, relative standard deviation; SRM, standard reference material.

Table 1. Properties of 20 Florida soil samples used in this study.

Soil great groups	Cation-exchange capacity	Clay <2 μm	Silt 2–50 μm	Sand 50–2000 μm	Organic C	pH H ₂ O
	cmol(+) kg ⁻¹		g kg ⁻¹			
Quartzipsamments (no coating)	1.33 \pm 0.51c†	3.8 \pm 1.3c	4.8 \pm 7.0b	992 \pm 8a	3.0 \pm 1.5b	5.4 \pm 1.2a
Quartzipsamments (slightly coated)	5.33 \pm 1.91bc	15.5 \pm 1.7bc	12.8 \pm 6.2b	972 \pm 5ab	8.2 \pm 3.0b	4.8 \pm 0.7a
Quartzipsamments (coated)	5.28 \pm 2.06bc	21.8 \pm 3.2b	40.3 \pm 16.1ab	938 \pm 6ab	11.7 \pm 4.0b	5.1 \pm 0.6a
Alaquods	11.0 \pm 5.69a	10.8 \pm 5.6bc	39.3 \pm 34.6b	950 \pm 34b	22.7 \pm 13.9a	4.6 \pm 0.3a
Paleudults	8.28 \pm 3.93ab	48.3 \pm 22.3a	76.5 \pm 38.8a	867 \pm 51c	12.2 \pm 6.2ab	5.4 \pm 0.4a

† Means within a column followed by the same letter are not significantly different ($P < 0.05$) using the Student *t*-test.

(Paudyn and Smith, 1992). This procedure was modified by Ammons et al. (1995) for analyzing metals in soils with >45% sand. In the modified method, HF was added to the solid 16 h before the aqua regia addition and the mixture was then subjected to microwave heating.

All three digestion methods, that is, hotplate aqua regia and microwave aqua regia with or without HF, are commonly used as total or pseudo-total soil digestion methods by different researchers in environmental studies, especially in European countries. However, those methods are not widely used in the USA for analyzing soils and NIST (National Institute of Standards and Technology, Gaithersburg, MD) standard reference materials (SRMs), partially due to the establishment of the USEPA methods (Chen and Ma, 1998). The accuracy and precision of those methods in determining elemental concentrations in soils might vary with element, soil properties, digestion method, as well as origin of the soils (anthropogenic vs. natural deposits). For example, aqua regia digestion might give close results for the maximum levels of polluting metals such as Cd, Cu, Pb, and Zn in soils (Marr et al., 1995), while metals like Ba, Cr, and Ni could be efficiently recovered only by using HF digestion (Sawhney and Stilwell, 1994). Florida soils were formed primarily from sandy marine sediments and typically consisted of >870 g kg⁻¹ sand (Table 1). These soils are prone to leaching and have extremely low baseline metal concentrations compared with soils from other parts of the world (Chen et al., 1999). Thus, great elemental recovery should be sought during method selection (Chen and Ma, 1998). The objectives of this study were (i) to compare the accuracy and precision of the three above-mentioned digestion methods in determining concentrations of different elements using three SRMs, and (ii) to study the variations in soil properties using 20 Florida sandy soils. It is hoped that such information will help to determine how the European regulatory methods work in analyzing trace metals in American soils and NIST SRMs. It will also assist scientists worldwide to choose the most appropriate technique for analyzing trace-metal concentrations in soils.

MATERIALS AND METHODS

Three SRMs (2704, 2709, and 2711) from NIST, representing river sediment, sandy soil, and contaminated soil, respectively, and 20 representative Florida soils were used in this study. The 20 Florida soils were randomly selected from pools of three dominant great groups occurring in Florida: Alaquods (Spodosols), Quartzipsamments (Entisols), and Paleudults (Ultisols). Because coating (kaolinite, hydroxy-interlayered

vermiculite, gibbsite, Fe oxyhydroxides, etc.) status could critically influence reactivity and metal retention, Quartzipsamments were selected such that samples with clean sand grains (<1% silt + clay), slightly coated grains (1–5% silt + clay), and coated grains (>5% silt + clay) were equally represented (Harris et al., 1996). Thus there were three groups of Quartzipsamments and one group each of Alaquods and Paleudults, with each group containing four soil samples (Table 1).

Microwave digestions were performed in a CEM MDS-2000 microwave oven (Matthews, NC). For aqua regia digestion, a sample to be analyzed needs to be randomly drawn from a well-mixed sample of 0.5000 g and weighed into a 120-mL Teflon-PFA microwave digestion vessel, then 12 mL of freshly prepared aqua regia solution (1/3 HNO₃-HCl, v/v) was added. The samples were digested at 0.69×10^6 Pa for 5.5 min, then filtered through Whatman no. 42 filters, transferred to 100-mL volumetric flasks, and diluted with deionized, distilled water (DDW). For aqua regia + HF digestion, 4 mL of concentrated HF were added to the soil sample and were allowed to react overnight at room temperature. Following the initial reaction period, 12 mL of aqua regia were added to the sample. The samples were then digested at 0.83×10^6 Pa (120 psi) for 20 min. After the digestion, 2 g of boric acid were added to neutralize excess HF before analysis. The samples were then filtered through Whatman no. 42 filters and diluted to 100 mL with DDW.

Conventional aqua regia digestion was performed in 250-mL glass beakers covered with watch glasses. A well-mixed sample of 0.5000 g was digested in 12 mL of aqua regia on a hotplate for 3 h at 110°C. After evaporation to near dryness, the sample was diluted with 20 mL of 2% (v/v with H₂O) nitric acid and transferred into a 100-mL volumetric flask after filtering through Whatman no. 42 paper and diluted to 100 mL with DDW.

Nitric acid, HCl, HF, and H₃BO₃ of trace-metal grade and standard solutions of Ca, Mg, K, P, Al, Fe, As, Ba, Cd, Cr, Cu, Pb, Mn, Ni, Se, and Zn were obtained from Fisher Scientific (Fair Lawn, NJ). Working standards were prepared daily by dilution from the stock solutions with digestion blanks. Instrument calibration standards were obtained from Spex Industries (Edison, NJ). Aluminum, Ba, Ca, Fe, K, Mg, Mn, P, and Zn were analyzed on a multi-channel Jarrell-Ash ICP-OES 61-E unit. Arsenic, Cd, Cr, Cu, Ni, Pb, and Se were determined on a Perkin-Elmer SIMAA6000 GFAAS unit. Each NIST SRM was digested in four replicates. In the stage of digestion, four quality-assurance samples (a blank, a duplicate, a spike, and an SRM) were included with every 20 soil samples (Chen, 1997). More (30%) quality-control samples (analytical blanks and calibration standards) were included in the determination of elemental concentrations in the digestion solution using either an ICP-OES or a GFAAS (Chen, 1997).

Precision was defined as relative standard deviation (RSD), which was calculated as a percentage using the standard deviation divided by the mean of replicated samples. Accuracy was determined by comparing the measured concentration with

the certified value and was expressed as percentage recovery (%R). Based on a Florida Department of Environmental Protection-approved research quality-assurance plan, satisfactory precision and accuracy were required to be within $\leq 20\%$ and 80 to 120% for all elements, respectively, which corresponded to the uncertainty of the NIST-certified values, according to a 95% confidence interval for the true values (Chen, 1997). In the present study, both accuracy and precision for all elements analyzed by the ICP-OES and GFAAS were acceptable, with matrix spike recovery being 90–110% and precision being $<15\%$.

All statistical analyses were performed using a PC version of the SAS program (ASA Institute, 1987). Analysis of variance was used to assess significant differences between treatments using a simple paired *t*-test at a confidence level of $\alpha = 0.05$. Simple correlation analysis was used to determine method correlation coefficients for each element at probability levels of $\alpha = 0.1$, 0.01, and 0.001, respectively.

Percent biases were used to compare magnitude and consistency of these methods for analyzing individual metals. The bias between hotplate and microwave aqua regia digestion methods was defined as the concentration difference between the two methods divided by the concentration of the hotplate digestion. As such, a positive bias between the two methods implied that the concentration obtained from the microwave aqua regia digestion was greater than that from the hotplate aqua regia digestion. The bias between the microwave aqua regia and aqua regia + HF digestion was defined similarly.

RESULTS AND DISCUSSION

Precision of Three Digestion Methods in Analyzing 16 Elements in NIST SRMs

Both hotplate and microwave aqua regia digestion achieved precise analysis using the three SRMs for all 16 elements except As in SRM 2704 by microwave and Se in SRM 2704 by both hotplate and microwave methods, which were out of the target precision range of $\leq 20\%$ (Table 2). Poor precision for Se in SRM 2704 may be attributed to low Se concentration (1.16 mg kg^{-1}) in the sample (Berrow and Stein, 1983; Binstock et al., 1990), which is $19.3\times$ the detection limit for Se

(0.06 mg kg^{-1}) using GFAAS. This will possibly make a relatively large contribution to imprecision of the analysis. Also, chemical interference due to volatilization losses for highly volatile elements include Pb, Cd, Zn, As, and Se is problematic for GFAAS (Sawhney and Stilwell, 1994), and is possibly another reason that contributed to the poor precision of As and Se in SRM 2704. For both digestion methods, four elements (Al, K, Cd, and Ni) showed relatively large RSD% ($>10\%$) in addition to As and Se, whereas seven elements, Ca, Fe, Mg, P, Mn, Pb, and Zn, showed excellent precision ($<5\%$) for all three SRMs. This is generally consistent with results reported by Nieuwenhuize et al. (1991), who indicated that RSD values for Fe, Mn, Pb, and Zn were $<12\%$ when using microwave aqua regia digestion.

In a comparison of hotplate to microwave aqua regia digestion, hotplate aqua regia digestion produced higher precision for As, Cr, and Se, which is unexpected, whereas microwave aqua regia digestion produced higher precision for Fe, Mg, and Ni for all three SRMs. Millward and Kluckner (1989) reported greater improvements in precision for the refractory and silica-bound elements such as Fe and Mg with the microwave method when comparing the two methods, which is consistent with our data (Table 2). However, when based on the average precision of the two digestion methods over 16 elements using three SRMs, the hotplate (4.6%) was slightly better than microwave aqua regia digestion (5.2%, Table 2). This implies that the two digestion procedures generally achieved comparable and acceptable precision in analyzing the 16 elements.

Satisfactory precision was achieved for all elements in all three NIST SRMs by using the microwave aqua regia + HF digestion, except Cd in SRM 2709 (22% RSD) (Table 2), which had much lower certified value (0.35 mg kg^{-1}) than SRMs 2704 (3.45 mg kg^{-1}) and 2711 (41.7 mg kg^{-1}) (Table 3). The low Cd concentration plus possible volatilization losses of Cd by the GFAAS determination (Sawhney and Stilwell, 1994) would make SRM 2709 perform differently from the other two

Table 2. Precision (as relative standard deviation %) of three digestion procedures for determination of 16 elements in three National Institute of Standards and Technology standard reference materials (NIST SRMs).

Element	Hotplate aqua regia				Microwave aqua regia				Microwave aqua regia + HF			
	2704	2709	2711	Avg.†	2704	2709	2711	Avg.	2704	2709	2711	Avg.
	%											
Al	5.5	11	6.7	7.4	14	3.8	2.0	6.6	2.1	1.4	1.0	1.2
Ca	0.4	1.0	2.3	0.9	1.5	0.6	0.3	0.8	1.1	1.1	1.0	1.1
Fe	0.9	1.9	4.2	2.3	0.3	1.6	0.7	0.9	1.9	1.2	1.3	1.5
K	12	7.6	4.1	7.6	19	5.6	3.0	9.2	1.4	1.2	1.6	1.4
Mg	1.3	2.4	3.1	2.3	0.5	1.1	0.5	0.7	1.1	1.2	0.8	1.0
P	1.3	4.0	2.7	2.7	0.7	5.1	1.1	2.3	0.9	3.0	1.0	0.6
As	4.2	1.0	2.1	2.4	25	6.4	2.7	11	7.9	6.5	1.5	5.3
Ba	2.0	1.9	3.5	2.5	1.9	2.2	1.7	1.9	1.7	1.3	1.3	1.4
Cd	7.7	13	1.8	7.5	4.6	10	6.2	6.9	8.1	22	5.9	12
Cr	2.3	6.7	4.6	4.5	7.7	7.4	8.2	7.7	4.5	8.5	1.3	4.7
Cu	2.5	5.9	3.7	4.0	2.8	1.1	1.0	1.6	7.6	9.0	0.5	5.7
Mn	0.4	1.2	3.1	1.6	0.9	1.4	0.5	0.9	0.5	1.2	1.0	0.9
Ni	20	2.5	9.1	11	5.1	0.4	5.7	3.7	13	1.5	7.2	7.2
Pb	1.7	4.9	1.6	2.7	4.5	3.5	6.1	4.7	1.4	2.8	3.2	2.5
Se	22	8.3	4.1	11	31	11	6.4	16	14	4.2	7.5	8.6
Zn	0.5	2.6	3.2	2.1	3.4	0.8	0.5	1.6	4.0	2.0	0.7	2.3
Average‡	5.3	4.7	3.7	4.6	8.7	3.9	2.9	5.2	4.5	4.3	2.3	3.7

† Average precision over three NIST SRMs (2704, 2709, and 2711) for each digestion procedure (four replications).

‡ Average precision over 16 elements for each SRM.

Table 3. Certified concentrations and recoveries and biases obtained using three digestion procedures with three National Institute of Standards and Technology (NIST) standard reference materials (SRMs).

Element	Certified concentrations			Recovery									Bias							
				Hotplate aqua regia			Microwave aqua regia			Microwave aqua regia + HF			Hotplate vs. microwave aqua regia				Microwave aqua regia vs. aqua regia + HF			
	2704	2709	2711	2704	2709	2711	2704	2709	2711	2704	2709	2711	2704	2709	2711	Mean	2704	2709	2711	Mean
	mg g ⁻¹																			
Al	60.9	75.2	65.2	27	43	33	60	55	45	95	92	94	127	28	34	60	57	69	111	79
Ca	26.0	18.9	28.8	103	87	81	102	87	84	102	102	100	-1	1	4	1	0	18	19	12
Fe	41.1	35.1	28.9	81	85	78	87	89	84	91	82	82	7	5	7	6	5	-8	-3	-2
K	19.8	20.3	24.6	13	22	21	55	30	30	97	95	96	335	34	40	136	77	221	223	174
Mg	12.0	15.1	10.5	81	93	77	92	97	83	91	90	89	14	5	8	9	-1	-7	7	0
P	1.01	0.64	0.82	90	94	85	96	100	92	94	101	93	7	7	8	7	-2	1	1	0
	mg kg ⁻¹																			
As	23.4	17.7	105	70	87	96	76	97	85	86	105	85	8	13	-12	3	13	8	1	7
Ba	414	967	727	24	42	28	46	45	32	93	89	91	95	7	16	39	103	96	184	128
Cd	3.45	0.35	41.7	75	87	83	90	89	89	96	115	87	19	3	7	10	7	29	-2	11
Cr	135	130	47.1	69	64	58	72	59	59	89	66	77	5	-8	1	-1	24	13	32	23
Cu	114	34.6	114	82	94	91	96	106	95	110	113	98	18	13	4	12	14	7	4	8
Mn	555	538	638	87	86	76	89	89	81	105	82	82	3	3	6	4	18	-7	1	4
Ni	44.1	88.0	20.6	103	90	87	92	89	87	91	80	79	-10	-1	0	-4	-2	-10	-10	-7
Pb	161	18.9	1162	79	64	83	99	68	91	95	88	90	25	6	10	14	-4	30	-1	8
Se	1.16	1.56	1.54	112	96	85	80	95	90	119	109	104	-29	-2	7	-8	49	15	15	26
Zn	438	106	350	97	91	90	95	97	92	95	113	95	-2	6	3	2	0	17	3	7
Avg. of each SRM				75	76	72	83	81	76	97	95	90								
Avg. of each digestion method				74			80			94										

SRMs. The precision for all elements was close to 5%, except for Cd, Ni, and Se, which were analyzed by GFAAS. High precision for analyzing As, Al, Ca, Cr, Cu, Fe, Mg, Mn, P, Pb, and Zn in marine sediments using this method has been reported by Paudyn and Smith (1992). Compared with the microwave aqua regia digestion procedure, the microwave aqua regia + HF procedure improved precision for more than one-half of the 48 analyses (16 elements \times 3 SRMs) (Table 2). The former method provided better precision for Mg, Ni, and Zn, and the latter for Al, K, Ba, and Pb. In addition, the average precision for the microwave aqua regia + HF digestion over 16 elements (3.7%) was better than the microwave aqua regia (5.2%) and the hotplate digestion method (4.6%, Table 2). This is consistent with the results of Marr et al. (1995) and Kackstaetter and Heinrichs (1997). They reported that in most cases the RSD values for both aqua regia digestion procedures were quite low, rarely >6% (Marr et al., 1995). Exceptions were observed for Pb, with \approx 7% error, and As, with >12% error, due to their volatile characteristics (Kackstaetter and Heinrichs, 1997).

Accuracy of Three Digestion Methods for Analyzing 16 Elements in NIST SRMs

National Institute of Standards and Technology SRMs are well-characterized, stable, homogeneous materials having one or more physical or chemical properties determined within stated measurement uncertainties to be used for the calibration of an apparatus or the assessment of a measurement method. To obtain the certified values, sample preparation procedures were designed to effect complete dissolution by NIST. If volatile elements (i.e., As, Se) were to be determined, precautions were taken in the dissolution of SRMs to avoid volatilization losses (NIST, 1995). Generally speaking, accurate results (80–120% recovery) were obtained for all elements except for Al, K, Ba, and Cr by the hotplate and micro-

wave aqua regia digestion methods using all three SRMs (Table 3). Our results were consistent with Kackstaetter and Heinrichs (1997), who indicated that aqua regia digestion provided satisfactory recovery for most base metals, partial recovery for Ba and Cr, and limited recovery for Al and K. Low Al and K recovery (<75%) in river sediments and NIST SRM 1645 by hotplate aqua regia digestion was also reported by Krause et al. (1995). Both Al and K may be components of silicate structures and they are thus relatively resistant to aqua regia, possibly leading to their low recovery. Marr et al. (1995) and Medved et al. (1998) noted that the efficiency of aqua regia in dissolving Ba in sediments or soils depended on its binding strength to insoluble minerals.

Low Cr recovery from soil and other materials has been attributed to the presence of insoluble Cr minerals such as chromspinel and chromite (FeCr_2O_4), and aqua regia was inefficient in dissolving these minerals (Liu et al., 1996; Medved et al., 1998). Low Cr recovery from river sediments AGAL-10 and AGAL-11 by both hotplate (\approx 36%) and microwave (\approx 43%) aqua regia digestions has been reported (Siaka et al., 1998). Low Cr recoveries (\approx 23–74%) from standard and sewage-sludge-amended soils have also been reported (Heydron and Damsgaard, 1995).

Compared with hotplate aqua regia digestion, microwave aqua regia digestion increased elemental recovery for all elements except Cr, Ni, and Se (Table 3). Such improvement was especially obvious for Al, K, Ba, Cd, Cu, and Pb as reflected by their relatively large positive biases (10–136%). In addition, the average recovery over 16 elements for the microwave aqua regia (79.9%) was slightly greater than that of the hotplate aqua regia (74.3%) digestion procedure (Table 3). The high efficiency of the sample digestion using the microwave method has been attributed to fragmentation of the solid materials due to the high pressures, which exposed fresher and finer portions of the sample to acid attack

(Nadkarni, 1984). Significantly higher values were found by Nieuwenhuize et al. (1991) for Cr and Fe in SRMs after microwave aqua regia digestion than hotplate aqua regia digestion. Paudyn and Smith (1992) noted that for many nonvolatile elements, the two methods provide similar recovery except for Al, whose recovery was greater using the microwave digestion, which is consistent with our result (Table 3).

Accurate results were obtained for all elements except Cr and Ni in three SRMs using the microwave aqua regia + HF digestion (Table 3). Low Cr recoveries in NIST SRMs 2709, 2710, and 2711 (75–89%) using microwave HNO₃–HF digestion (Wu et al., 1996) and in USGS standard rocks using microwave aqua regia + HF digestion have been reported (Nadkarni, 1984; Lamothe et al., 1986). A sequential extraction study on industrially contaminated soil indicated that both Cr and Ni were mainly associated with the residual fractions (Davisson et al., 1998). Medved et al. (1998) found that Cr is bound to insoluble minerals such as chromspinel and chromite in soils. As indicated by Marr et al. (1995), even aqua regia + HF digestion was inefficient in dissolving these minerals. However, complete recoveries for Cr and Ni from marine and river sediments by microwave aqua regia + HF digestion have been reported (Rantala and Loring, 1989) and were attributed to a strong dissolution technique being adopted (i.e., more acid and longer heating times) (Bettinelli et al., 1987). Similar results for Cr from NIST SRM 2704 were reported when using microwave HNO₃–HF–HClO₄ digestion (Liu et al., 1996). The authors noted that satisfactory performance could be achieved if the element was present in a relatively labile form, which was consistent with our results in the case of river sediment NIST SRM 2704 (≈89% for Cr and ≈91% for Ni respectively, Table 3). For the other two NIST SRMs (2709 and 2711), however, incomplete dissolution of Cr (≈66–77%) and

Ni (≈79–80%) minerals was obtained (Table 3), which implies that Cr and Ni in the two standard soils may be present as insoluble minerals.

Compared with the microwave aqua regia digestion (Table 3), microwave aqua regia + HF digestion improved accuracy for Al, Ca, K, As, Ba, Cr, Cu, Se, and Zn in the three SRMs, as reflected by their large positive biases and the closeness to the certified values (Table 3). These results are consistent with a sequential extraction study of Ca, Fe, Cr, Mn, Pb, and Zn in sediments by Mahan et al. (1987), who indicated that an overall superior recovery of metals was obtained by using the aqua regia + HF digestion. Among the three digestion procedures, as expected, microwave aqua regia + HF digestion achieved the overall best average elemental recovery (94%) for 16 elements in three SRMs followed by the microwave (80%) and hotplate (74%) aqua regia digestions (Table 3). Our results are consistent with those of Kokot et al. (1992) who demonstrated statistically that aqua regia + HF was the preferable procedure for digesting NIST SRM 2704. Among the three SRMs tested, SRM 2711 showed the lowest average recovery (79%) over 16 elements using three digestion methods, whereas SRMs 2704 (85%) and 2709 (84%) showed comparable recovery (Table 3).

Comparison of Three Digestion Procedures for Analyzing 16 Elements in Florida Soils

Average Elemental Concentrations Based on 20 Florida Soils

Greater values of all elements except for Ca, P, Cd, and Se were obtained in the 20 Florida soils using microwave rather than hotplate aqua regia digestion. The most notable were K, Cr, Cu, and Ni as reflected by their large positive biases (>116%, Table 4). However,

Table 4. Comparison of three digestion methods for determination of 16 elements in 20 Florida soils.

Element	Hotplate vs. microwave aqua regia						Microwave aqua regia vs. aqua regia + HF		
	Hotplate aqua regia	Microwave aqua regia	Microwave aqua regia + HF	Bias	Correlation (<i>r</i>)	<i>t</i> -test‡	Bias	Correlation (<i>r</i>)	<i>t</i> -test
	mg g ⁻¹			%			%		
Al	2.05 ± 2.60†	2.98 ± 4.35	2.28 ± 2.45	45	0.98***	*	-30	0.52*	NS
Ca	0.30 ± 0.33	0.29 ± 0.34	0.31 ± 0.33	-5	0.85***	NS§	7	0.76***	NS
Fe	0.84 ± 0.92	1.10 ± 1.09	1.10 ± 0.72	30	0.97***	*	1	0.67**	NS
K	0.03 ± 0.03	0.08 ± 0.06	0.12 ± 0.11	143	1.00***	*	62	1.00***	*
Mg	0.08 ± 0.06	0.10 ± 0.09	0.10 ± 0.06	38	0.97***	*	-2	0.83***	NS
P	0.09 ± 0.21	0.11 ± 0.24	0.10 ± 0.22	15	0.89***	NS	-4	0.83***	NS
mg kg ⁻¹									
As	0.32 ± 0.28	0.40 ± 0.38	0.44 ± 0.44	23	0.82***	NS	10	0.82***	NS
Ba	10.4 ± 24.4	12.6 ± 28.0	13.2 ± 16.6	21	1.00***	*	5	0.96***	*
Cd	0.04 ± 0.12	0.07 ± 0.15	0.07 ± 0.14	12	0.95***	NS	-1	0.87***	NS
Cr	2.44 ± 2.48	5.30 ± 4.50	13.9 ± 22.4	117	0.71***	NS	162	0.52*	NS
Cu	0.92 ± 1.20	2.36 ± 1.74	3.66 ± 2.08	157	0.72***	NS	55	0.62**	*
Mn	28.0 ± 40.5	33.7 ± 40.2	39.0 ± 35.5	20	0.98***	NS	16	0.94***	NS
Ni	2.27 ± 1.60	6.15 ± 5.34	14.5 ± 8.92	171	0.03 NS	NS	136	0.58**	NS
Pb	2.81 ± 1.76	3.81 ± 2.10	2.91 ± 1.97	36	0.87***	*	-24	0.94***	*
Se	0.06 ± 0.06	0.05 ± 0.04	0.11 ± 0.10	-9	0.42*	NS	128	0.57**	NS
Zn	2.66 ± 1.52	4.65 ± 2.57	16.6 ± 3.81	75	0.86***	*	257	0.69***	*

* Significant at the 0.05 probability level.

** Significant at the 0.01 probability level.

*** Significant at the 0.001 probability level.

† Arithmetic mean ± standard deviation.

‡ Paired *t*-test (least significant difference) at $\alpha = 0.05$.

§ NS = not significant.

significant improvement in digestion efficiency was only observed for Al, Fe, K, Mg, Ba, Pb, and Zn, when using a simple *t*-test at $\alpha = 0.05$. This indicates that with the help of the microwave procedure, aqua regia was more effective in dissolving these elements from Florida surface soil horizons than was open digestion. Smaller, lower volatilization losses of elements with the microwave technique than the hotplate is possibly another reason. In addition, analytical results for the GFAAS determination of As, Cd, Cr, Cu, Ni, Pb, and Se provided low acid blank values for Cd and Pb. This is consistent with Chakraborty et al. (1996), who reported that the microwave digestion procedure should be used when the risk of environmental pollution is high. Similarly, significantly greater recoveries of Cr and Fe from Dutch soils were obtained using the microwave technique than using the hotplate aqua regia digestion (Nieuwenhuize et al., 1991). The biases for concentrations of Ca and Se between the two digestion procedures were negligible ($<10\%$) (Table 4).

The microwave aqua regia + HF digestion procedure produced greater concentrations of K, Cr, Cu, Ni, Se, and Zn, and smaller concentrations of Al and Pb in the 20 Florida soils than did the microwave aqua regia digestion procedure. Concentrations of Ca, Fe, Mg, P, As, Ba, Cd, and Mn were comparable (with bias $<20\%$) using the two microwave methods (Table 4). However, paired *t*-tests indicate significant improvement in digestion efficiency were observed only for K, Ba, Cu, and Zn. Lamothe et al. (1986) noted that Pb recovery from geological samples using HCl-HNO₃-HF digestion depended on sample texture.

Significant positive correlation coefficients were found for all elements except for Ni in 20 Florida soils between the two aqua regia digestion procedures and between the two microwave digestion procedures (Table 4). This suggests that similar biases between these methods would be expected if they were used to determine concentrations of these 16 elements in other Florida soils (except for Ni). For example, on average, $\approx 21\%$ more Ba was released by the microwave than the hotplate aqua regia digestion and $\approx 62\%$ more K was released by the microwave aqua regia + HF than the aqua regia digestion for Florida soils (Table 4). The discrepancy in elemental recovery of Ni among the three methods may be attributed to certain soil matrices, such as chromite, aluminosilicate minerals, and organic matrix, which cannot be decomposed by either aqua regia or aqua regia + HF (Wen et al., 1997; Wu et al., 1996). However, further investigation is needed to identify the possible soil matrices that exist in Florida soils.

The biases between hotplate and microwave aqua regia digestion procedures for the three NIST SRMs, compared with the microwave aqua regia and aqua regia + HF digestion procedures for 20 Florida soils for the 16 elements, were obviously different. Greater biases were obtained between the first two methods for elements Fe, Mg, As, Cr, Cu, Mn, Ni, Pb, and Zn and lower biases for elements Al and Ba in the 20 Florida soils than the three NIST SRMs (Tables 3 and 4). On the other hand, greater biases were obtained between

the second two methods for elements Cr, Cu, Ni, Se, and Zn and lower biases for elements Al, K, Ba, and Pb in the 20 Florida soils than in the three SRMs (Tables 3 and 4). The NIST SRMs were ground finer (100 mesh for SRM 2704 and <200 mesh for SRMs 2709 and 2711) than the Florida soils (60 mesh), and that probably improved the overall precision of the analysis for those materials. In addition, soil properties are important in determining elemental recovery during digestion. Elemental recovery may vary from soil to sediment and other material, even using the same digestion procedure. Otherwise, biases between different digestion procedures in NIST SRMs and Florida soils should be comparable.

Average Elemental Concentrations of 20 Florida Soils in Five Groups

To better understand how elemental concentrations vary with soil properties and digestion method, concentrations of 16 elements in 20 soils of five great groups were determined using the three aqua regia digestion methods (Table 5). Based on how elemental concentrations changed with the three digestion methods and soil properties, the 16 elements can be divided into four groups.

Elemental concentrations in the first group, including Cr, Cu, K, Mn, Ni, and Zn, increased in all five types of soils as the digestion method became more aggressive, that is, from hotplate aqua regia to microwave aqua regia to microwave aqua regia + HF (Table 5). The increases were often large and easily observed. For example, mean Cr concentrations in the slightly coated Quartzipsamments increased from 1.52 to 5.39 to 16.9 mg kg⁻¹, respectively. This implies the importance in selecting an appropriate digestion method to determine elemental concentrations in soils. In addition, suitable SRMs play an essential role in evaluating the accuracy of new analytical methods and maintaining the quality of established measurement procedures. In the beginning of soil digestion, inclusion of a SRM with similar properties and elemental concentrations to the soils to be determined should also be emphasized as implied from the bias differences between SRMs and Florida soils (Tables 3 and 4). Theoretically, SRM 2709 (a sandy soil) should have similar elemental recovery to Florida soils, but elemental recoveries from SRM 2709 by different digestion methods provided no similarity to those of Florida soils. For example, unlike Florida soils, Cr recoveries from SRM 2709 remained almost constant, changing from 64 to 59 to 66% as the digestion method became more aggressive (Table 3). The low Cr concentrations (maximum of 32.6 mg kg⁻¹ in the Ultisol) and the possible relatively soluble Cr minerals in Florida soils compared with SRM 2709 (130 mg kg⁻¹) plus the fine grinding sample may have been the primary reason for the discrepancy.

Elemental concentrations in the second group of elements, including Al, Ca, Fe, Mg, and Ba, generally increase as the three digestion methods became more aggressive in four groups of soils (the Alaquods and the

Table 5. Comparison of three digestion procedures for determining elemental concentrations in five different soil groups in Florida.

	Al	Ca	Fe	K	Mg	P	As	Ba	Cd	Cr	Cu	Pb	Mn	Ni	Se	Zn
Method	mg g ⁻¹							mg kg ⁻¹								
	Quartzipsammments, <i>n</i> = 4 (no coating, averaging 4 mg g ⁻¹ clay)															
Aqua regia hotplate	0.12 [†]	0.073	0.18	0.005	0.014	0.003	0.19	0.60	0.031	1.45	0.34	1.30	6.30	2.65	0.059	1.13
Microwave aqua regia	0.10	0.077	0.44	0.012	0.017	0.005	0.15	0.98	0.004	3.76	1.71	2.42	14.9	3.35	0.013	1.69
Microwave aqua regia + HF	0.13	0.091	0.82	0.015	0.020	0.007	0.12	1.73	0.015	7.26	3.09	1.01	22.2	12.6	0.072	14.1
	Quartzipsammments, <i>n</i> = 4 (slightly coated, averaging 18 mg g ⁻¹ clay)															
Aqua regia hotplate	1.24	0.23	0.63	0.028	0.073	0.040	0.18	2.25	0.011	1.52	1.75	2.90	23.3	1.69	0.005	2.67
Microwave aqua regia	1.56	0.27	0.73	0.061	0.10	0.035	0.23	3.30	0.041	5.39	3.15	3.62	27.2	9.50	0.041	4.96
Microwave aqua regia + HF	2.13	0.26	1.08	0.14	0.11	0.040	0.37	7.68	0.065	16.9	3.96	3.01	42.7	16.3	0.093	20.1
	Quartzipsammments, <i>n</i> = 4 (coated, averaging 21 mg g ⁻¹ clay)															
Aqua regia hotplate	2.47	0.11	1.04	0.05	0.09	0.065	0.42	8.00	0.013	2.25	0.75	3.10	42.0	2.23	0.073	3.00
Microwave aqua regia	3.20	0.15	1.24	0.12	0.12	0.073	0.40	10.8	0.075	4.51	2.41	4.53	50.9	4.64	0.058	5.81
Microwave aqua regia + HF	3.30	0.18	1.04	0.19	0.13	0.066	0.46	14.4	0.082	7.25	3.06	3.52	43.1	11.2	0.15	18.3
	Alaquods, <i>n</i> = 4 (averaging 13 mg g ⁻¹ clay)															
Aqua regia hotplate	0.24	0.44	0.14	0.010	0.048	0.043	0.16	3.25	0.007	0.80	0.50	1.74	2.50	1.81	0.018	2.25
Microwave aqua regia	0.38	0.32	0.29	0.036	0.052	0.050	0.32	3.58	0.052	2.61	0.82	2.16	5.40	5.47	0.050	3.39
Microwave aqua regia + HF	0.44	0.51	0.65	0.063	0.062	0.054	0.29	6.75	0.020	5.42	2.64	1.48	15.2	15.9	0.045	13.6
	Paleudults, <i>n</i> = 4 (averaging 38 mg g ⁻¹ clay)															
Aqua regia hotplate	6.21	0.66	2.22	0.07	0.15	0.32	0.66	37.8	0.15	6.18	1.25	5.01	66.0	2.98	0.12	4.25
Microwave aqua regia	9.63	0.62	2.78	0.16	0.22	0.38	0.89	44.5	0.20	10.1	3.70	6.33	70.4	7.79	0.090	7.39
Microwave aqua regia + HF	5.42	0.49	1.92	0.22	0.18	0.35	0.95	35.6	0.18	32.6	5.56	5.51	71.9	16.6	0.21	16.9

[†] Mean value for four soils in each group.

Quartzipsamments) but not in the Paleudults. For the Paleudults, elemental concentrations of the second group increased as digestion methods changed from hotplate to microwave aqua regia; however, they decreased unexpectedly as the digestion methods changed from microwave aqua regia to aqua regia + HF (Table 5). The difference between the latter two digestion procedures was the addition of HF, with a longer reaction time and a higher temperature, which was intended to aid in the decomposition of Al-Si minerals (Nadkarni, 1984; Quevauviller et al., 1993). The effectiveness of HF in decomposing Al-Si minerals was demonstrated in the three SRMs as reflected by the mean bias of +79% in Al concentrations between the microwave aqua regia and aqua regia + HF digestion methods (Table 3). In addition, the mean total Al concentrations in the three SRMs (67.1 mg g⁻¹, Table 3) were approximately 28 times greater than the mean total Al concentrations in the 20 Florida soils (2.44 mg g⁻¹, Table 4). The extremely high quartz contents (identified by x-ray diffraction) in the 20 Florida soils probably made them behave differently from the three SRMs. Paleudults contained relatively high Al concentrations (Table 5) compared with the other four soil groups and extremely high quartz contents compared to the three SRMs, which may have caused significant Al concentration reductions in the presence of HF. It was possible that a mixture of Al-Si-F minerals precipitated during the digestion process (Hingsten et al., 1972). It was also possible that Ca, Fe, Mg, and Ba coprecipitated with the Al-Si-F minerals, thus reducing their concentrations (Table 5). However, no minerals except quartz were identified by x-ray diffraction in the residuals of the Paleudults after microwave aqua regia + HF digestion (data not shown).

Lead is the only element of the third group. Its concentrations in all soil groups increased as the digestion method changed from hotplate to microwave aqua regia

digestion. But it decreased as the digestion method changed from microwave aqua regia to aqua regia + HF (Table 5). It seemed that total decomposition using microwave aqua regia + HF method would underestimate total Pb concentrations in Florida soils. This was also confirmed by the paired t-tests at $\alpha = 0.05$ (Table 4). Yet such a pattern was not observed for the three SRMs (Table 3). It is speculated that formation of Pb₂SiO₄ may have caused the reduction in Pb concentrations using the microwave aqua regia + HF digestion. Generally speaking, Pb₂SiO₄ is a relatively soluble Pb mineral and thus is not normally present in soils (Lindsay, 1979). However, in the presence of HF and under high temperature and pressure, larger amounts of SiO₂ may have been dissolved to form SiO₄⁴⁻ to react with Pb²⁺ to form Pb₂SiO₄. Since Pb concentrations in Florida soils were <4 mg kg⁻¹ (Table 4), it was not possible to identify this mineral in the residual fraction after digestion. Wen et al. (1997) suggested that the low Pb recovery from sediment SRM 280 after aqua regia + HF digestion is possibly due to PbCl₂ formation, which also had a low solubility. No pattern was observed in concentration changes with the three digestion methods for elements in the fourth group including P, As, Cd, and Se. There is possibly the problem of the detection limits and sensibility of the instruments used to determine the elemental concentrations (P, As, and Se). At a low concentration range (<50× the detection limits), it is hard to determine the improvement of either precision or accuracy of the analysis by varying digestion procedures.

CONCLUSIONS

Precise analysis was achieved for most of the 16 target elements, except for As, Se, and Cd from three different NIST SRMs (2704, 2709, and 2711) by the three commonly used aqua regia digestion procedures: hotplate

aqua regia, microwave aqua regia, and microwave aqua regia + HF. The microwave aqua regia method was comparable in both precision and accuracy with the hotplate aqua regia method for analyzing most of the target elements except for the silicate-binding metals, such as Al, Ba, and K, whose dissolution was slightly greater using microwave digestion. The microwave aqua regia + HF method achieved satisfactory recoveries for all elements except for Cr and Ni in the three NIST SRMs.

In terms of method correlation coefficients and elemental recoveries of the target elements in 20 Florida surface soils, microwave aqua regia improved digestion efficiency for Al, Fe, K, Mg, Ba, Pb, and Zn, when using *t*-tests at $\alpha = 0.05$. Microwave aqua regia + HF improved results (at the $\alpha = 0.05$ level) only for K, Ba, Cu, and Zn, but not for the other 12 elements. However, according to the digestion efficiency in 20 different Florida soils, the elements were separated into four groups: Group 1 (K, Cr, Cu, Ni, Mn, and Zn), Group 2 (Al, Ca, Fe, Mg, and Ba), Group 3 (Pb), and Group 4 (P, As, Cd, and Se). The microwave aqua regia + HF procedure underestimated total concentrations of Group 3 in all 20 Florida soils and total concentrations of Group 2 in four Florida Paleodults.

ACKNOWLEDGMENTS

This research was sponsored in part by the Florida Center for Solid and Hazardous Waste Management (Contract No. 96011017). The helpful corrections to the manuscript of this article by Drs. F.E. Smith, A. Mallarino, and three anonymous reviewers are gratefully acknowledged.

REFERENCES

- Ammons, J.T., M.E. Essington, R.J. Lewis, A.O. Gallagher, and G.M. Lessman. 1995. An application of a modified microwave total dissolution technique for soils. *Commun. Soil Sci. Plant Anal.* 26: 831-842.
- Berrow, M.L., and W.M. Stein. 1983. Extraction of metals from soils and sewage by refluxing with *aqua regia*. *Analyst* 108:277-285.
- Bettinelli, M., U. Baroni, and N. Pastorelli. 1987. Analysis of coal fly ash and environmental materials by inductively coupled plasma atomic emission spectrometry: Comparison of different decomposition procedures. *J. Anal. At. Spect.* 2:485-489.
- Binstock, D.A., P.M. Grohse, A. Gaskill, Jr., K.K. Luk, P.L. Swift, H.M. Kingston, and C. Sellers. 1990. Validation of methods for determining elements in solid waste by microwave digestion. p. 259-270. *In* D. Friedman (ed.) *Waste testing and quality assurance*. Vol. 2. American Society for Testing and Materials, Philadelphia, PA.
- Chakraborty, R., A.K. Das, M.L. Cervera, and M. de la Guardia. 1996. Literature study of microwave-assisted digestion using electrothermal atomic absorption spectrometry. *Fres. J. Anal. Chem.* 35: 99-111.
- Chen, M. 1997. Research quality assurance plan for background concentrations of trace metals in Florida surface soils. QAPP 960117. Soil Water Sci. Dep., Univ. Florida, Gainesville, FL.
- Chen, M., and L.Q. Ma. 1998. Comparison of four EPA digestion methods for metal analysis using certified and Florida soils. *J. Environ. Qual.* 27:1294-1300.
- Chen, M., L.Q. Ma, and W.G. Harris. 1999. Concentrations of 15 metals in Florida surface soils. *J. Environ. Qual.* 28:1173-1181.
- Davison, C.M., A.L. Duncan, D. Littlejohn, A.M. Ure, and L.M. Garden. 1998. A critical evaluation of the three-stage BCR sequential extraction procedure to assess the potential mobility and toxicity of heavy metals in industrially-contaminated land. *Anal. Chim. Acta.* 363:45-55.
- Harris, W.G., R.D. Rhue, G. Kidder, R.B. Brown, and R. Littell. 1996. Phosphorus retention as related to morphology of sandy coastal plain soil materials. *Soil Sci. Soc. Am. J.* 60:1513-1521.
- Heydron, K., and E. Damsgaard. 1995. Indirect determination of soluble trace elements in certified reference materials by neutron activation analysis. *Mikrochim. Acta* 119:297-304.
- Hingsten, F.J., A.M. Posner, and J.P. Quirk. 1972. Anion adsorption by goethite and gibbsite: I. The role of the proton in determining adsorption envelopes. *J. Soil Sci.* 23:177-192.
- Kackstaetter, U.R., and G. Heinrichs. 1997. Validity of low cost laboratory geochemistry for environmental applications. *Water Air Soil Pollut.* 95:119-131.
- Kokot, S., G. King, H.R. Keller, and D.L. Massart. 1992. Microwave digestion: An analysis of procedures. *Anal. Chim. Acta.* 259:267-279.
- Krause, P., B. Erbsloh, R. Niedergesab, R. Pepelinik, and A. Prange. 1995. Comparative study of different digestion procedures using supplementary analytical methods for multielement-screening of more than 50 elements in sediments of the river Elbe. *Fres. J. Anal. Chem.* 35:3-11.
- Kubrakova, I. 1997. Microwave-assisted sample preparation and pre-concentration for ETAAS. *Spectrochim. Acta, B* 52:1469-1481.
- Lamothe, P.J., T.L. Fries, and J.J. Consul. 1986. Evaluation of a microwave oven system for the dissolution of geologic samples. *Anal. Chem.* 58:1881-1886.
- Lindsay, W.L. 1979. *Chemical equilibria in soils*. John Wiley & Sons, New York.
- Liu, J., R.E. Sturgeon, V.J. Boyko, and S.N. Willie. 1996. Determination of total chromium in marine sediment reference material BCSS-1. *Fres. J. Anal. Chem.* 35:416-419.
- Mahan, K.I., T.A. Foderaro, T.L. Garza, R.M. Martinez, G.A. Maroney, M.R. Trivisonno, and E.M. Willging. 1987. Microwave digestion techniques in the sequential extraction of calcium, iron, chromium, manganese, lead, and zinc in sediments. *Anal. Chem.* 59:938-945.
- Marr, I.L., P. Kluge, L. Main, V. Margerin, and C. Lescop. 1995. Digests or extracts?—Some interesting but conflicting results for three widely differing polluted sediment samples. *Mikrochim. Acta* 119:219-232.
- Medved, J., V. Stresko, J. Kubova, and J. Polakovicova. 1998. Efficiency of decomposition procedures for the determination of some elements in soils by atomic spectroscopic methods. *Fres. J. Anal. Chem.* 36:219-224.
- Millward, C.G., and P.D. Kluchner. 1989. Microwave digestion technique for the extraction of minerals from environmental marine sediments for analysis by inductively coupled plasma atomic emission spectrometry and atomic absorption spectrometry. *J. Anal. At. Spect.* 4:709-713.
- Nadkarni, R.A. 1984. Applications of microwave oven sample dissolution in analysis. *Anal. Chem.* 56:2233-2237.
- Nieuwenhuize, J., C.H. Poley-Vos, A.H. van den Akker, and W. van Delft. 1991. Comparison of microwave and conventional extraction techniques for the determination of metals in soils, sediment and sludge samples by atomic spectrometry. *Analyst* 116:347-351.
- Niskavaara, H., C. Reimann, V. Chekushin, and G. Kashulina. 1997. Seasonal variability of total and easily leachable element contents in topsoils (0-5 cm) from eight catchments in the European arctic (Finland, Norway, and Russia). *Environ. Pollut.* 96:261-274.
- NIST. 1995. *Environmental inorganic standard reference materials*. National Institute of Standards and Technology, Philadelphia, PA.
- Paudyn, A.M., and R.G. Smith. 1992. Microwave decomposition of dusts, ashes, and sediments for the determination of elements by ICP-AES. *Can. J. Applied Spect.* 37:94-99.
- Quevauviller, P., J. Imbert, and M. Olle. 1993. Evaluation of the use of microwave oven systems for the digestion of environmental samples. *Mikrochim. Acta* 112:147-154.
- Rantala, R.T.T., and D.H. Loring. 1989. Teflon bomb decomposition of silicate materials in a microwave oven. *Anal. Chim. Acta* 220:263-267.
- Ryss, I.G. 1956. *The chemistry of fluorine and its compounds*. State Publishing House for Scientific, Technical, and Chemical Literature.

- ture, Moscow. (English translation U.S. Atomic Energy Commission translation Series AEC-tr-3927.)
- SAS Institute. 1987. SAS user's guide: Statistics. SAS Inst., Cary, NC.
- Sawhney, B.L., and D.E. Stilwell. 1994. Dissolution and elemental analysis of minerals, soils and environmental samples. p. 49–82. *In* J.E. Amonette and L.W. Zelazny (ed.) Quantitative methods in soil mineralogy. SSSA, Madison, WI.
- Siaka, M., C.M. Owens, and G.F. Birch. 1998. Evaluation of some digestion methods for the determination of heavy metals in sediment samples by flame-AAS. *Anal. Lett.* 31:703–718.
- Smith, F.E., and E.A. Arsenault. 1996. Microwave-assisted sample preparation in analytical chemistry. *Talanta* 43:1207–1268.
- Vercoutere, K., U. Fortunati, H. Muntau, B. Griepink, and E.A. Maier. 1995. The certified reference materials CRM 142 R light sandy soil, CRM 143 R sewage sludge amended soil and CRM145 R sewage sludge for quality control in monitoring environmental and soil pollution. *Fres. J. Anal. Chem.* 352:197–202.
- Wen, X., L. Wu, Y. Zhang, and Y. Chu. 1997. Optimized microwave preparation procedure for the elemental analysis of aquatic sediment. *Fres. J. Anal. Chem.* 357:1111–1115.
- Wu, S., Y. Zhao, X. Feng, and A. Wittmeier. 1996. Application of inductively coupled plasma mass spectrometry for total metal determination in silicon-containing solid samples using the microwave-assisted nitric acid-hydrofluoric acid-hydrogen peroxide-boric acid digestion system. *J. Anal. At. Spect.* 11:287–296.

Stabilization of Fertilizer Nitrogen-15 into Humic Substances in Aerobic vs. Waterlogged Soil Following Straw Incorporation

Olivier C. Devêvre and William R. Horwáth*

ABSTRACT

This study was undertaken to investigate and quantify the interactive effects of flooding and straw incorporation on key microbial processes, principally stabilization of fertilizer N into various soil organic matter (SOM) pools. The fate of fertilizer ^{15}N in a paddy soil was examined at 5, 15, and 25°C, with and without rice (*Oryza sativa* L.) straw added, and under flooded and nonflooded conditions. After a 160-d incubation, three fractions of the SOM were separated and defined as directly alkali-extractable humic substances (DAEHS), reducible metal-bound humic substances (RMBHS), and non-alkali-extractable organic matter (NAEOM). The DAEHS had the highest percentage, up to 50%, of fertilizer ^{15}N recovered at 160 d, indicating that this SOM fraction was the most dynamic fraction of the SOM. On the other hand, the RMBHS is considered the least dynamic pool, containing up to 12% fertilizer ^{15}N after 160 d. The NAEOM was surprisingly highly enriched, up to 28% fertilizer ^{15}N , and showed a significant treatment effect, suggesting that some active components of N cycling were present in this SOM fraction. The addition of rice straw increased the recovery of fertilizer ^{15}N in the above SOM fractions. Flooding significantly reduced the stabilization of fertilizer N compared with the nonflooded treatment. Indices of recalcitrance of the stabilized N confirm that the soil N supply capacity does not decrease with flooding. The total alkali-extractable organic matter (AEOM = DAEHS + RMBHS), as the NAEOM, appears to be a complex and dynamic mixture of potentially mineralizable and recalcitrant forms of N. Our data show that long-term N availability and stabilization into humic fractions is a function of rice residue input and temperature; however, the effects of residue and temperature are inversely related. With increase in temperature of incubation, less fertilizer N becomes stabilized into humic fractions, presumably from increased microbial activity, microbial consumption of potential humic precursors (N-containing precursors of humic substances turned over faster at higher temperatures), and/or formation of different end-products with less humification potential.

NITROGEN is the most growth-limiting nutrient in rice cropping systems (Savant and DeDatta, 1982). The fate of N in rice soils is often directly related to manage-

ment of fertilizers and crop residues. In rice systems, management activities, such as fertilization and residue management, affect losses of N through volatilization and denitrification activity (Aulakh et al., 1992). In addition, N added to the soil as fertilizers or crop residues is immobilized by the soil biomass and subsequently transformed into organic forms that may be relatively resistant to mineralization (Broadbent and Nakashima, 1974; Olson and Swallow, 1984). The availability of stabilized organic N in rice cropping systems is not well known. Better understanding of the behavior of added N fertilizer and the availability of N from the soil organic N is essential for developing efficient N management strategies to enhance and sustain rice production.

Rice is the second most important crop in the world (Food and Agriculture Organization of the United Nations, 1996), and its production yields a large amount of straw residues annually. Management of these residues is required for seedbed preparation, maintaining soil fertility, and weed and pest management. Open-field burning, which has been used traditionally to dispose of residues and sanitize fields against pests and diseases, has become unpopular in many regions of the world because of air pollution concerns. The incorporation of straw residues into the soil combined with winter flooding has been proposed as an alternative to open-field straw burning in California Sacramento Valley and might also become common in other rice systems in the temperate zone. The effect of incorporating straw on long-term fertility in rice cropping systems has not received a great deal of attention to date.

Declining yield in continuously cropped irrigated rice systems where a significant portion of the rice residue

O.C. Devêvre and W.R. Horwáth, University of California, Department of Land, Air and Water Resources, One Shields Ave., Davis, CA 95616-8627. Received 10 Jan. 2000. *Corresponding author (wrhorwath@ucdavis.edu).

Published in Soil Sci. Soc. Am. J. 65:499–510 (2001).

Abbreviations: AEOM, alkali-extractable organic matter; ANOVA, analysis of variance; CFI, chloroform-fumigation-incubation; DAEFA, directly alkali-extractable fulvic acids; DAEHA, directly alkali-extractable humic acids; DAEHS, directly alkali-extractable humic substances; IRRI, International Rice Research Institute; NAEOM, non-alkali-extractable organic matter; PLSD, protected least significant difference; PMN, potentially mineralizable N; PRRI, Philippines Rice Research Institute; RMBFA, reducible metal-bound fulvic acids; RMBHA, reducible metal-bound humic acids; RMBHS, reducible metal-bound humic substances; SOM, soil organic matter.