

Multi-element Analysis of Tinishu Akaki River Sediment, Ethiopia, by ICP-MS after Microwave Assisted Digestion

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Abstract

This work describes a method for multi-element analysis of cadmium, cobalt, chromium, copper, manganese, nickel, lead and zinc in Tinishu Akaki River sediment, Ethiopia, by inductively coupled plasma mass spectrometry. River sediment samples were collected between November 2002 and January 2003 for the first campaign, and between November 2003 and January 2004 for the second campaign. The samples were kept frozen until they were lyophilized, grounded in a mortar and pestle and sieved. A fraction less than 63 μm was taken for the analysis. Different acid combinations were investigated for the digestion of sediment samples: HCl/HNO_3 , $\text{HClO}_4/\text{HNO}_3$ and $\text{HF}/\text{HCl}/\text{HNO}_3/\text{H}_3\text{BO}_3$ in a microwave digestion system. Complete dissolution of materials was achieved with the latter. Optimum values for instrumental parameters of the ICP-MS were sought and set up. Multi-element standard solutions were used for the calibration of the procedure. The methodology and accuracy was evaluated by the analysis of certified reference materials of sedimental origin. Very low limits of detection were obtained for all elements, which were less than $0.65 \mu\text{g g}^{-1}$, except for Zn, which was $2.8 \mu\text{g g}^{-1}$. Good precision, with relative standard deviations better than 7% for most of the elements, was found.

Keywords: Heavy metals, Tinishu Akaki River, sediment, microwave acid digestion, ICP-MS, Ethiopia

Résumé

Nous décrivons dans ce travail une méthode multiélément permettant l'analyse de cadmium, cobalt, chrome, cuivre, manganèse, nickel, plomb et zinc dans les sédiments de la rivière Tinishu Akaki en Éthiopie, grâce à la spectrométrie à plasma inductif couplée à celle de

masse. Les échantillons de sédiment de la rivière ont été récoltés lors de deux campagnes d'échantillonnage de novembre 2002 à janvier 2003 et de novembre 2003 à janvier 2004. Les échantillons ont été conservés congelés jusqu'aux étapes de lyophilisation, broyage et passage au crible. La fraction inférieure à 63 μm a été retenue pour analyse. Nous avons testé plusieurs combinaisons d'acides pour la digestion des sédiments, soit: HCl/HNO_3 , $\text{HClO}_4/\text{HNO}_3$ et $\text{HF}/\text{HCl}/\text{HNO}_3/\text{H}_3\text{BO}_3$ dans un digesteur micro-ondes. La minéralisation complète des solides a pu être obtenue avec le dernier mélange d'acides. Nous avons recherché et ajusté les paramètres instrumentaux du ICP-MS aux conditions optimales. Nous avons utilisé des solutions standards multiéléments pour la procédure de calibration. Nous avons évalué la méthodologie par l'analyse de matériaux standards certifiés de sédiment qui ont montré une bonne exactitude. Nous avons obtenu de très basses limites de détection, moindre que $0.65 \mu\text{g g}^{-1}$ pour tous les éléments, sauf le Zn à $2.8 \mu\text{g g}^{-1}$. Nous avons mesuré avec bonne précision, avec des écarts-types relatifs inférieurs à 7% pour la plupart des éléments.

Introduction

Concern over the possible ecological effect of the increasing accumulation of metallic contaminants in the environment is growing. For this reason, the investigation of heavy metals in sediments is essential since even slight changes in their concentration above the acceptable levels, whether due to natural or anthropogenic factors, can result in serious environmental and subsequent health problems (1-12).

Domestic and industrial wastes, atmospheric emissions, metal corrosion products and leached agricultural chemicals (13) are the most important sources of pollution. These wastes are either directly discharged into the TAR (Tinishu Akaki River) or into the streams flowing into the TAR without being treated. These inputs have led

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to an important increase in the sediment trace metal concentrations in the receiving water body. Trace elements are good markers to understand sources contributing to the pollution at a particular site.

In a previous paper (14), the trace metal concentrations of the water of TAR have been reported. It was found that significant pollution levels exist for some of the investigated metals, indicating intense anthropogenic pollution sources that are found in the river and its tributaries.

The interest of analyzing sediment samples for their contents in metals lies in the fact that they constitute concentrated reservoirs of these analytes, exhibiting higher concentrations than other adjacent samples, such as water, plants, *etc* (15). Sediment samples have the ability to reflect the water quality and can be used for the assessment of river pollution particularly for trace elements (16). Moreover, sediments conserve important environmental information and are increasingly recognized as both a sink and a possible source of contaminants in aquatic systems as a result of the local physicochemical conditions (9, 13, 17-23).

To determine metal concentrations in sediment samples, the metals must be extracted prior to quantitative analysis. The use of microwave assisted treatments in a closed vessel is nowadays an attractive way of sample dissolution especially because it is fast, safe and has a minimum potential for contamination (3) compared to conventional digestion procedures, such as wet digestion and dry ashing, which is often the most time consuming stage of the analysis. In order to be effective, the digestion treatment of the sample must ensure a complete dissolution of the matrix to allow the release of the analytes in a chemical form compatible with the analytical method (24).

Considering the matrix of most environmental samples such as sediment, soil and sludge, a total digestion scheme must include the use of HF acid to completely release the trace elements from the aluminosilicate phase (25). There are currently various standard methods for the analysis of sediments, which employ different acid mixtures and microwave heating techniques (10). For the digestion of sediment mixtures, HNO_3/HCl (26), $\text{HNO}_3/\text{H}_2\text{O}_2/\text{HF}$ (27), $\text{HNO}_3/\text{HClO}_4$ (28), $\text{HNO}_3/\text{HCl}/\text{HF}/\text{H}_3\text{BO}_3$ (24) and $\text{HNO}_3/\text{HClO}_4/\text{HF}/\text{H}_2\text{O}_2$ (8) have been mainly used. Without HF added to the sample, the recovery of the elements, which may be present in significant concentration within the silicate-aluminosilicate matrix, may be incomplete (11). The digestion method proposed in this study included $\text{HNO}_3/\text{HCl}/\text{HF}/\text{H}_3\text{BO}_3$ and avoided

the complications mentioned above.

Inductively Coupled Plasma-Mass Spectrometry (ICP-MS), Electrothermal-Atomic Absorption Spectrometry (ET-AAS), Inductively Coupled Plasma-Atomic Emission Spectrometry (ICP-AES) and Neutron Activation Analysis (NAA) are among the most commonly used analytical techniques for the determination of trace elements in sediments. Due to its multi-element capability, high sensitivity, ability to provide accurate and precise results, high detection power, low sample consumption and spectral simplicity, ICP-MS has become a valuable instrumental techniques for trace element analysis (11, 13, 27).

This paper reports the development of a microwave assisted digestion procedure for dissolution of sediment samples followed by determination of trace elements by ICP-MS. The purpose of the this work is to investigate the input of polluting elements, to determine the concentrations of Cd, Co, Cr, Cu, Mn, Ni, Pb and Zn concentrations and to estimate the degree of pollution in the sediment samples collected from various sites along the TAR and its tributaries.

STUDY AREA

Geography

Addis Ababa, the capital city of Ethiopia, is located in the heart of the country. It is the country's commercial, manufacturing, and cultural center. Cement, leather and beverage are among the industrial activities in the city. Addis Ababa has grown at an astonishing speed since it was established in 1886. Today, it has a population of more than three million in a land area of 540 sq km, of which 18.2 are rural, and it lies between 2200 and 2500 meters above sea level on the Central Ethiopian Plateau. Geographically, it is located at 9°N and 38°E. The city rambles pleasantly across many wooden hillsides and gullies cut through with fast flowing streams, especially during the rainy seasons from July to September (29). Tinishu Akaki river basin covers the Western part of the city (Fig. 1). Geologically, Addis Ababa lies on volcanic rocks ranging in composition from rhyolitic to basaltic types. The main stratigraphic units are constituted by basaltic, rhyolitic, trachytic and trachy-basaltic lava flows and welded tuffs found at different localities and ages (30).

Climate

Despite its proximity to the equator, Addis Ababa enjoys a mild, Afro-Alpine temperate and warm temper-

ate climate. The lowest and the highest annual average temperature are between 10 and 25°C. April and May are the driest months. The main rainy season occurs between mid June and mid September, which is responsible for 70% of the annual average rainfall of 1400 mm. It is characterized by intense rainfall of short duration. During the dry season the days are pleasantly warm and the nights are cool. During the rainy season both days and nights are cool (31).

Experimental

Instrumentation

ICP-MS

The instrument used was a Perkin Elmer Sciex Elan 5000 ICP-mass spectrometer (Perkin-Elmer, Überlingen, Germany) equipped with quartz torch, nickel sampler and skimmer cones, a peristaltic pump (maintaining a 1 ml

min⁻¹ sample uptake rate), a cross-flow type pneumatic nebulizer and a double pass Scott-type spray chamber. Operating conditions are summarized in Table 1.

Microwave digestion system

For the dissolution of samples, a microwave digestion system (MLS-1200 MEGA, Milestone, USA) with MDR (Microwave Digestion Rotors) technology was used with TFM (Tetrafluoromethaxil) vessels.

Reagents and standard solution

The reagents used were all analytical–reagent grade, unless stated otherwise. Water was doubly distilled and further purified using a Milli-Q water purification system (Millipore, USA). 40% HF and 70% HClO₄ were obtained from Merck (Germany), while 65% nitric and 32% hydrochloric acids were purified by sub-boiling distillation in quartz equipment.

Saturated boric acid solution was prepared by adding 7 g of boric acid (UCB, Belgium) to 100 mL of Milli-Q water into a clean Teflon bottle. The boric acid in the sealed bottle was allowed to dissolve with heat on a hot plate in a fume hood. Once dissolved, crystals formed in the bottle on cooling and the solution was ready to use. A small volume of saturated boric acid was used to prevent insoluble fluorides in acid dissolutions.

Analytical multi-element standard solutions were prepared by diluting single and multi-element standard solution (Merck) containing 1g L⁻¹ metal ions for ICP-MS. A stock internal standard solution 10 mg L⁻¹ of In, Sc and Tl each was prepared from single-element standard solutions (1g L⁻¹) for ICP-MS. Where necessary, standards and samples were diluted with 0.14 M HNO₃.

Sampling and pre-treatment of samples

After surveying the study area, a total of 23 sites were selected for bottom sediment sampling, 16 within

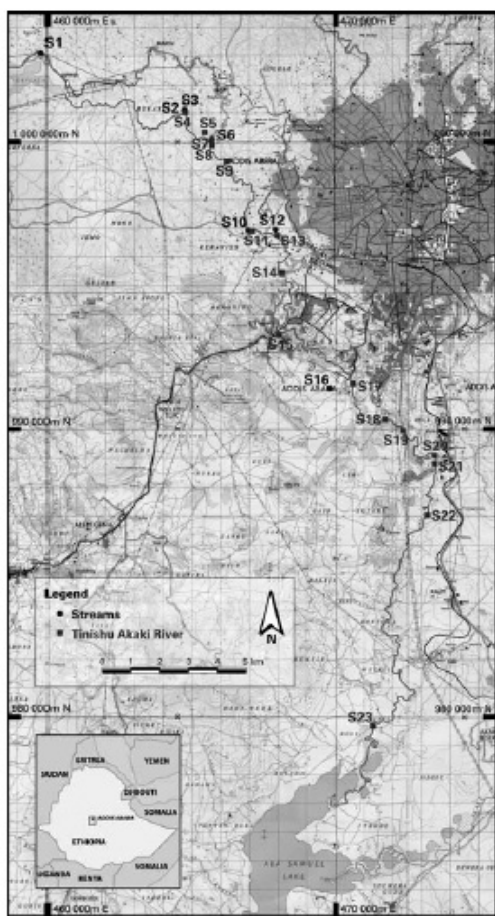


Figure 1. Location of sampling sites in Tinishu Akaki River and its tributaries, Ethiopia.

Table 1. ICP-MS operating conditions.

RF power (W)	1000
Plasma argon, L min ⁻¹	15
Nebulizer flow, L min ⁻¹	0.9 - 1
Nebulizer	Cross flow
Data acquisition	Peak hop transit
Resolution	Normal
Dwell time (ms)	50
Number of replicates	3

the TAR and 7 along the streams that enter into TAR. The positions of the sampling sites were determined using a differential Global Positioning System (GPS) with at least 4 satellites (3-D). The study area and the location of sampling stations are shown in Figure 1. To assess anthropogenic impacts, some samples were collected both upstream and downstream from the urban and industrial areas. Stations for the collection of river sediment samples include locations along some of the tributaries that enter the river as well as the main stem of the river. Samples of river sediment from twenty-three sampling stations along the Tinishu Akaki River and its tributaries were collected during the period between December 2002 to January 2003 for the first campaign, and between November 2003 to January 2004 for the second campaign. A composite sampling technique was employed. At each sampling location, a total of about 500 gram of sediment sample was taken at several spots from the bottom of the river 0 – 20 cm depth using a hand held polyethylene spoon (VWR international, Belgium). For the shallow and deeper part of the river, a sampling station equipped with a cable-operated stainless steel Van-Veen grab sampler (Eijkelkamp, The Netherlands) that had been pre-cleaned in the laboratory and with water was used. Following collection, sediment samples were carefully removed from the sampler and outer parts, which are in contact with the stainless steel body of the sampler, were removed using a polyethylene spoon to prevent contamination. After that, the sediment sample was transferred to 500 mL wide-mouthed polyethylene bottles (VWR international, Belgium). Shortly after sampling, sediment samples were stored frozen. The storage and preservation of sediment samples were described elsewhere by Bartram and Balance (32). Finally, the preserved samples were transported to the Laboratory of Analytical Chemistry, Belgium.

For sample preparation, each composite sample was lyophilized. Then, it was grinded in a mortar and pestle and sieved through a nylon grid. The fraction with particle size less than $63\mu\text{m}$ was preserved for analysis since pollutants are largely bound to silt/clay particles. This was done in order to minimize the variability due to grain size composition (33). Finally, it was stored in polyethylene bottles.

Sample digestion procedure

Of the powered sieved grain, size fraction 0.25 g was weighed directly into each pre-cleaned vessel and various acid combinations were added (Table 2). Then, the vessels were placed inside a rotor of the microwave

digestion system, sealed, tightened using a torque wrench and finally submitted to a microwave dissolution program (Table 2). For procedure A (HNO_3/HCl) and B ($\text{HNO}_3/\text{HClO}_4$), after only cooling the digest was filtered to remove the silica content through an ashless 90 mm dia. Whattmann type 41 filter paper (England) and quantitatively transferred to a polyethylene bottle and diluted with Milli-Q water to 50 mL. In the case of procedure C ($\text{HNO}_3/\text{HCl}/\text{HF}/\text{H}_3\text{BO}_3$), after cooling the samples, 2 mL of saturated boric acid solution was added, the vessel was re-capped, returned to the oven, and heated at 300 watts for 3 minutes. At this stage, the clear solution obtained from the sediments was quantitatively transferred into a 50 mL calibrated flask and diluted to volume with Milli-Q water. A vessel containing the same acid mixture as used for the samples was adopted for controlling the analytical blank. The digests were stored at 4°C until analysis.

Analytical procedure for trace element analysis by ICP-MS

The performance of an ICP-MS instrument strongly depends on the operating conditions (11). The plasma operating conditions such as the nebulizer flow rate, the position of the torch, RF power, and the ion lens voltages of the instrument were optimized while continuously nebulizing $50\mu\text{g L}^{-1}$ of the multi-element standard solution of Be, Co, Rh, In, Pb and Tl so as to maximize the ^{103}Rh and ^{115}In signals. The ion lens voltages were chosen each time and the sampler and skimmer were replaced and/or cleaned. The plasma operating conditions were selected to obtain a good compromise between high sensitivity and low oxide levels.

For ICP-MS measurements, 0.2 mL of the digest sample was pipetted into a 10 mL polyethylene tube. Then $50\mu\text{L}$ of 10 mg L^{-1} Sc, In and Tl were added as an internal standard and the volume was adjusted to 10 mL with 0.14 M HNO_3 , resulting in a 50-fold dilution. The measurements for the blank, the $100\mu\text{g L}^{-1}$ multi-element standard containing the same amount of acids and the internal standard mix containing Sc, In and Tl were also carried out. The sample solution was quantified by external calibration, that is, by comparing the net signals against those of multi-element standards. The following analysis sequence was applied: first the blank, then several samples and only at the end of the sequence, the standard. The blank intensity was subtracted from both the standard and the sample intensities.

Table 2. Operating condition for microwave digestion procedures.

Step	Reagents	Volume (mL)	Power (W)	Hold Time (min.)
Procedure A				
1	HCl	6	250	2
2	HNO ₃	2	400	2
3			500	10
Vent			0	5
Procedure B				
1	HClO ₄	1	250	5
2	HNO ₃	5	500	5
3			650	5
4			350	10
5			0	5
Vent				
Procedure C				
1	HCl	6	250	8
2	HNO ₃	2	400	4
3	HF	2	600	6
4			0	2
5	H ₃ BO ₃	2	300	3
6			0	2
Vent			0	5

Results and Discussion

Analytical performance of digestion methods for certified reference materials

The reliability of the analytical methods was evaluated by means of the certified reference materials (BCR CRM 277 Estuarine sediment and BCR CRM 320 River sediment). The certified reference materials were obtained from the Community Bureau of Reference.

Three microwave digestion programs with three different acid combinations and volumes labeled as procedure A, B and C, shown in Table 2, have been examined for the digestion of two sediment reference materials to determine which was most efficient to extract metals from the samples tested.

The mean of the recoveries ($n = 4$) for each of the three acid combinations are shown in Tables 3 and 4. The recovery of each metal is calculated based on the mean certified value [(measured concentration ($\mu\text{g g}^{-1}$)/mean certified value ($\mu\text{g g}^{-1}$) $\times 100$]. In general, the HNO₃/HCl (34) and HNO₃/HClO₄ digestion procedures could not completely extract all the analytes from the matrices and this is confirmed by the present study. It was clearly

observed by the poorest recovery of Cr, in both CRMs, that it was mostly present in mineral form. Procedure A and B hardly extracted 90% of the Cr, while with procedure C the recovery increased up to about 95%. For the other elements, the recoveries by procedure A and C were quite acceptable. In the case of CRM 320, the mean recoveries increased from 86.3% and 81.6% for procedure A and B to 100.8% for procedure C. The increase for Cr was most spectacular, from 63.8% and 55.5% to 93.5%. This efficiency was expected since the sediment was completely dissolved by procedure C. No filtration was required.

The addition of HF strongly influenced the efficiency of microwave digestion for CRMs. This acid breaks down silicates and minerals better than HNO₃/HCl and HNO₃/HClO₄. However, HF can give rise to problems in instrumental analysis and sample preparation due to the erosion of glassware. Since the digestion requires HF, the smallest volume necessary should be used, such as the 1 – 2 mL used in this study (1). The additional treatment with 2 mL of a saturated boric acid solution in step 5 makes possible destruction of the excess of HF in order to avoid glassware and torch damage (3). As a matter of fact, diluting the initial solution by 50-fold could reduce the above-mentioned problem. Procedure C provided the best % recoveries and thus this program was chosen for use in further experiments to analyze sediment samples collected from the TAR and its tributaries.

Precision

The precision of the measurements (relative standard deviation, RSD) was evaluated from four different measurements on the two certified reference materials of sediment. The precision data are also listed in Tables 3 and 4. The precision obtained by ICPMS for CRM 277 was better than 6, 6, and 10% RSD for procedure A, B, and C, respectively. In the case of CRM 320, a precision of better than 6, 10 (except Cd, 21.7%) and 9% (except for Pb, 12%) were obtained for procedure A, B and C, respectively.

Accuracy

The accuracy of the analytical method was evaluated by analysis of certified reference materials and the recovery values summarized in Tables 3 and 4. They show a good agreement with the certified values. As discussed before, the mean recoveries, and thus accuracies, obtained for the digestion procedure C was about 100%. Owing to lower extraction efficiencies, especially for Cr and to a lesser extent for Co, Ni, Mn and Pb, the digestion

procedures A and B yielded values that were too low. It can be concluded that, on condition that a nearly quantitative extraction is achieved, such as with digestion procedure C, no systematic negative or positive results were obtained. Agreement within the 95% confidence interval of the certified values is reached.

Detection Limits

Limits of detection were estimated as the concentrations corresponding to three-times the standard deviation, σ , of the intensities of the blank signals at m/z for each analyte, where a blank $\text{HNO}_3/\text{HCl}/\text{HF}/\text{H}_3\text{BO}_3$ digestion procedure was assessed. The results are summarized in Table 5. The average values and the standard deviation of the blank signals were obtained by using the results of 10 replicate measurements of $\text{HNO}_3/\text{HCl}/\text{HF}/\text{H}_3\text{BO}_3$ digest and 5 measurements of $100 \mu\text{g L}^{-1}$ standards. The limits of detection for most elements were below $0.65 \mu\text{g g}^{-1}$ except for Zn, which was $2.8 \mu\text{g g}^{-1}$. Although a large dilution factor ($10,000\times$) was applied, these values were

low enough for the samples analyzed and were better than the values obtained by Bettinelli *et al.* (24), using the same instrument.

Analysis of Tinishu Akaki River (TAR) sediment samples

The optimized method was applied for the analysis of TAR sediment by ICP-MS after microwave-assisted digestion with $\text{HNO}_3/\text{HCl}/\text{HF}/\text{H}_3\text{BO}_3$. The results of TAR sediments and its tributaries, some freshwater sediment quality guidelines and some unpolluted sediment values are presented in Table 6.

As can be seen in Table 6, the elemental concentration of eight metals measured in sediment samples collected from the TAR were found to be in the range of $0.12 - 1.61$ (Cd), $16.9 - 70.6$ (Co), $60.9 - 16254$ (Cr), $23.7 - 117$ (Cu), $1200 - 6480$ (Mn), $46.9 - 201$ (Ni), $20.3 - 638$ (Pb) and $141 - 826$ (Zn) $\mu\text{g g}^{-1}$, respectively. From the mean values for all sampling points (Table 6), it appears that there is hardly a significant difference between the

Table 3. CRM 277 Estuarine Sediment reference material.

Element	Concentration ($\mu\text{g g}^{-1}$), 95 % C.I., d.w., (n = 4)						
	Certified value	HNO_3/HCl	% Recovery	$\text{HNO}_3/\text{HClO}_4$	% Recovery	$\text{HNO}_3/\text{HCl}/\text{HF}/\text{H}_3\text{BO}_3$	% Recovery
^{114}Cd	11.9 ± 0.4	11.6 ± 0.4	97.5	11.5 ± 0.4	96.6	11.8 ± 0.5	99.2
^{59}Co	(15 – 19.8)	15.03 ± 0.8	(86.4)	15.02 ± 0.2	(86.3)	15.6 ± 1.1	(89.7)
^{52}Cr	192 ± 7	175 ± 6	91.1	169.5 ± 4.4	88.3	189 ± 12	98.4
^{63}Cu	101.7 ± 1.6	101.0 ± 5.7	99.3	99.3 ± 5.6	97.6	103.3 ± 6.3	101.6
^{55}Mn	(1520 – 1620)	1573 ± 58	(100.2)	1458 ± 36	(92.9)	1592 ± 52	(101.4)
^{60}Ni	43.4 ± 1.6	42.9 ± 1.3	98.8	40.5 ± 1	93.3	44.6 ± 4.3	102.8
^{208}Pb	146 ± 3	148 ± 7	101.4	139 ± 8	95.2	145 ± 6	99.3
^{66}Zn	547 ± 12	535 ± 18	97.8	601 ± 12	109.9	545 ± 10	99.6
Mean	-	-	96.6	-	95	-	99

Table 4. CRM 320 River Sediment reference material.

Element	Concentration ($\mu\text{g g}^{-1}$), 95 % C.I., d.w., (n = 4)						
	Certified value	HNO_3/HCl	% Recovery	$\text{HNO}_3/\text{HClO}_4$	% Recovery	$\text{HNO}_3/\text{HCl}/\text{HF}/\text{H}_3\text{BO}_3$	% Recovery
^{114}Cd	0.533 ± 0.026	0.555 ± 0.029	104.1	0.460 ± 0.1	86.3	0.543 ± 0.011	101.9
^{59}Co	(17.3 – 22.1)	15.3 ± 0.5	(77.7)	15.1 ± 0.4	(76.6)	19.9 ± 1	(101)
^{52}Cr	138 ± 8	88 ± 3	63.8	76.6 ± 1.1	55.5	129 ± 9	93.5
^{63}Cu	44.1 ± 1	43.6 ± 2.3	98.9	46.2 ± 2.1	104.8	42.7 ± 3.6	96.8
^{55}Mn	(619 – 782)	639 ± 21	(91.2)	517 ± 14	(73.8)	745 ± 40	(106.4)
^{60}Ni	75.2 ± 1.4	60.8 ± 2.6	80.9	57.9 ± 4.6	77	74 ± 4	98.4
^{208}Pb	42.3 ± 1.6	37.3 ± 2.1	88.2	31.6 ± 1.3	74.7	44.9 ± 5.4	106.1
^{66}Zn	142 ± 3	122 ± 6	85.9	148.1 ± 14	104.3	145 ± 10	102.1
Mean	-	-	86.3	-	81.6	-	100.8

two sampling periods. Only for Cr, the mean value was 1.8 times higher during the first sampling campaign. A slightly lower mean obtained from the second campaign may be due to an increased rainfall during the days preceding the sampling.

Landajo *et al.* (35) have reported Cd concentrations in Asua, Galindo and Nerbioi-Ibaizabal River sediments, Spain, in the range of 1.2 – 381 $\mu\text{g g}^{-1}$. Mihai and Mather (18) have also reported the average Co, Cr, Cu, Ni and Zn concentrations in the Romanian sector of the Danube River and the Black Sea coast sediments as in the range of 6 – 9, 33 – 130, 8 – 170, 28 – 75 and 39 – 416 $\mu\text{g g}^{-1}$, respectively. Mn and Pb concentrations in sediment samples from the Pearl River system, China, have been reported as in the range of 646 – 1034 and 80 – 118 $\mu\text{g g}^{-1}$, respectively (12).

When compared to those concentrations, the present study in the TAR yields much higher values for Cr and Co and higher values for Mn and Ni. The Cd values are significantly lower in the TAR-sediment.

The results of the TAR-sediment can also be compared to those of the unpolluted sediment (15) for the elements Cd, Cu, Mn, Pb and Zn. It appears that the investigated sediment is strongly polluted with Pb and Zn and to a lesser extent with Cu and Cd (Table 6).

A better comparison can be made with the interim freshwater sediment quality guidelines for Cd, Cr, Cu, Pb and Zn. From the mean values in Table 6, it is obvious that the TAR sediments are highly polluted with Cr (35 to 70 times above the guideline). Furthermore, the mean values for Cu, Pb and Zn significantly exceed the guidelines. The mean Cd values are of the same order

as the guideline.

Some extremely high values were found, such as Cr at site S7 and S8 (more than 1%), and high values such as Cd, Cu, Pb and Zn at site S17. The highest Mn concentrations are found at sites S2, S13, and S15. Also, the earlier described analyses of the TAR-water samples, which were collected at the same locations, indicated very high concentrations primarily for Cr and Mn at sites downstream of the major anthropogenic sources.

The concentration of trace elements of TAR sediment shows a pattern of behavior linked to source contribution and anthropogenic activities around the river. The highest concentration of Cr were found at S7 and for Cd, Cu, Pb and Zn, the highest values were found at S17. This exemplify the influence of the direct waste discharge of industrial effluents from Addis Ababa Tannery and that of the battery factory, respectively, which are located upstream of S7 and S17. Moreover, TAR tributaries such as S6, S12 and S16 exert a major influence on the trace element chemistry of TAR sediment as they receive all kinds of wastes.

Manganese could result from the chemical erosion of the earth's crust and some industrial activities such as distilleries, battery factory, public and domestic waste, and especially from hospitals as permanganate is used as oxidizing agent. The probable sources of Cu in TAR could be from corrosion of metallic parts of vehicles, preservatives of leather and some agricultural fungicides. Also, the sources of cobalt in environmental samples could be from corrosion of metallic parts of vehicles.

Table 5. Detection Limit ($\mu\text{g g}^{-1}$) of the procedure for $\text{HNO}_3/\text{HCl}/\text{HF}/\text{H}_3\text{BO}_3$ microwave digestion.

Element	Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
DLs	0.01	0.01	0.58	0.15	0.64	0.18	0.58	2.8

Table 6. Bottom sediment trace metal concentrations, $\mu\text{g g}^{-1}$, in the Tinishu Akaki River.

Sam- pling Site	Latitude/ Longitude	Eleva- tion (m)	Cam- paign	Concentrations (95 % C.I.), d.w.							
				Cd	Co	Cr	Cu	Mn	Ni	Pb	Zn
S2	N09°03.507' E038°40.806'	2507	I	0.417 (0.058)	44.4 (0.6)	176.9 (5.4)	51.3 (1.3)	5081 (86)	103.5 (1.7)	26.0 (2.0)	186.7 (14.6)
			II	0.394 (0.054)	45.5 (1.8)	218.4 (4.9)	53.7 (2.3)	2917 (107)	110.4 (4.0)	27.54 (1.06)	176.7 (7.7)
S3	N09°03.491' E038°40.798'	2511	I	0.319 (0.003)	30.7 (0.7)	86.3 (1.1)	34.9 (1.3)	3205 (86)	67.7 (2.2)	22.07 (0.38)	141.1 (5.9)
			II	0.305 (0.026)	31.9 (0.8)	104.3 (3.2)	35.5 (1.3)	3655 (90)	65.8 (1.3)	21.78 (1.01)	141.9 (4.5)

Table 6 (Continued)

S4	N09°03.456' E038°40.821'	2511	I	0.305 (0.056)	41.0 (2.4)	89.3 (8.1)	23.7 (4.8)	3677 (228)	93.5 (6.0)	24.4 (2.1)	168 (14)
			II	0.378 (0.019)	34.8 (1.3)	132.4 (6.3)	40.5 (1.1)	3137 (122)	80.5 (3.1)	48.8 (2.1)	154.3 (5.7)
S5	N09°03.080' E038°41.188'	2467	I	0.213 (0.035)	39.5 (1.1)	112.8 (6.6)	57.5 (3.5)	3230 (114)	96.8 (3.1)	20.3 (1.1)	140.9 (8.7)
			II	0.334 (0.021)	35.9 (0.5)	142.9 (3.3)	44.4 (0.6)	2991 (60)	84.0 (1.3)	31.1 (2.4)	142.5 (3.0)
S6	N09°02942' E038°41.322'	2462	I	0.349 (0.068)	31.4 (0.9)	3129 (79)	93.0 (2.4)	2666 (65)	95.5 (3.1)	50.9 (0.8)	415.7 (18.6)
			II	0.348 (0.026)	37.5 (0.6)	584.6 (6.9)	59.1 (1.7)	2524 (49)	113.6 (2.3)	41.6 (1.3)	255.6 (7.9)
S7	N09°02.931' E038°41.317'	2464	I	0.281 (0.007)	17.0 (0.6)	15355 (327)	52.6 (1.7)	1971 (58)	47.3 (1.7)	82.4 (2.8)	159 (6.3)
			II	0.316 (0.057)	16.9 (0.5)	16254 (1337)	55.2 (1.8)	1344 (31)	53.5 (4.0)	125.0 (7.2)	183.9 (6.4)
S8	N09°02.829' E03841.329'	2455	I	0.349 (0.09)	24.9 (0.7)	15790 (320)	56.4 (0.3)	1986 (46)	66.4 (2)	59 (4.2)	174.0 (9.6)
			II	0.316 (0.024)	41.9 (1.7)	9311 (367)	55.4 (3.2)	2446 (95)	84.5 (4.9)	93.4 (7.8)	171.5 (8.2)
S9	N09°02.532' E038°41.615'	2428	I	0.537 (0.09)	26.3 (2.1)	15594 (1009)	54.7 (3.6)	1951 (136)	70.6 (4.9)	40.0 (3.9)	218.9 (17.9)
			II	0.355 (0.025)	41.7 (0.4)	1435 (13)	76.9 (0.9)	1693 (15)	103.4 (1.8)	40.1 (1.2)	177.9 (4.5)
S10	N09°01.233' E038°42.017'	2368	I	0.12 (0.021)	33.7 (1.0)	612.4 (18.3)	56.5 (1.8)	1916 (61)	129.8 (3.6)	22.8 (1.2)	152.7 (6.1)
			II	0.690 (0.022)	28.0 (0.4)	60.9 (0.8)	32.4 (1.4)	3551 (49)	52.2 (0.9)	53.9 (1.6)	198.9 (21.3)
S11	N09°01.220' E038°42.098'	2362	I	0.375 (0.017)	39.7 (1.6)	1587 (58)	52.9 (0.8)	2977 (108)	99.7 (3.8)	30.9 (1.4)	214.8 (15.1)
			II	0.360 (0.040)	34.8 (1.1)	1372 (37)	57.1 (1.6)	2670 (79)	99.8 (5.0)	27.8 (2.1)	171.9 (4.0)
S12	N09°01.248' E038°42.539'	2367	I	0.291 (0.026)	70.6 (2.3)	389.4 (27.8)	78.7 (3.9)	2642 (93)	200.6 (6.81)	40.3 (7.5)	222.2 (28.7)
			II	0.353 (0.033)	45.7 (1.6)	211.9 (11)	65.6 (2.0)	2048 (70)	139.3 (2.9)	40.8 (2.8)	192.3 (5.9)
S13	N09°01.134' E038°42.575'	2343	I	0.591 (0.07)	44.5 (1.7)	1106 (40)	64.4 (3.5)	6480 (816)	99.9 (4.3)	70.3 (3.2)	324.4 (14.8)
			II	0.405 (0.010)	39.2 (1.4)	506.6 (20.3)	61.1 (2.7)	4479 (158)	112.4 (6.2)	59.5 (6.4)	235.8 (9.0)
S14	N09°00.430' E038°42.656'	2327	I	0.413 (0.064)	37.6 (2.6)	376 (17)	85.9 (18.5)	3896 (132)	89.2 (3.5)	52.3 (7.1)	205.6 (9.8)
			II	0.389 (0.019)	31.3 (1.1)	597.5 (23.5)	45.6 (1.8)	3171 (117)	76.7 (3.5)	77.6 (2.9)	248.4 (34.2)
S15	N08°59.259' E038°42.607'	2313	I	0.532 (0.038)	34.0 (1.1)	330.1 (11.0)	40.0 (1.9)	6411 (196)	68.8 (3.0)	39.6 (4.7)	210.0 (6.9)
			II	0.621 (0.024)	33.7 (0.7)	472.9 (8.9)	37.9 (1.5)	3560 (72)	65.5 (2.9)	77.4 (2.7)	258.1 (5.5)

Table 6 (Continued)

S16	N08°58.243' E038°43.578'	2221	I	-	-	-	-	-	-	-	-
			II	0.736 (0.108)	33.1 (0.5)	157.6 (29.1)	76.2 (1.2)	1905 (19)	94.1 (5.2)	251.2 (9.2)	443.4 (21.3)
S17	N08°58.338' E038°44.008'	2224	I	1.613 (0.131)	27.8 (1.2)	161.3 (9.9)	117.2 (7.7)	1566 (72)	76.4 (3.9)	325.4 (24.6)	825.7 (38.8)
			II	1.047 (0.172)	36.3 (0.9)	236.8 (3.8)	111.7 (5.7)	1731 (46)	85.0 (4.9)	637.9 (27.8)	441 (10)
S18	N08°57.658' E038°44.623'	2194	I	0.919 (0.147)	29.2 (1.8)	136.4 (8.1)	65.7 (7.2)	1519 (106)	73.0 (4.9)	131.4 (11.3)	385.9 (29)
			II	0.640 (0.047)	28.4 (0.3)	180.9 (5.8)	58 (2)	1781 (17)	76 (2.4)	340.6 (13.4)	324.8 (3.9)
S19	N08°57.448' E038°44.961'	2215	I	1.036 (0.072)	26.3 (1.1)	135.8 (10.1)	74.3 (2.7)	1584 (68)	69.3 (2.9)	223.8 (19.1)	416.7 (14.4)
			II	0.563 (0.031)	27.8 (1.2)	137.6 (9.2)	73.8 (5.1)	1823 (68)	68.7 (4.9)	346.8 (19.8)	250 (11)
S20	N08°56.978' E038°45.562'	2201	I	0.941 (0.063)	23.5 (0.8)	209.7 (6.9)	69.0 (3.9)	1450 (38)	63.8 (1.9)	168.9 (10.2)	428.3 (28.4)
			II	0.368 (0.049)	17.0 (0.2)	95.6 (9.5)	29.3 (0.4)	1200 (18)	46.9 (3.2)	76.5 (5.4)	172.8 (0.4)
S21	N08°56.826' E038°45.562'	2194	I	0.669 (0.046)	20.4 (0.8)	198.8 (8.0)	64.3 (3.2)	1385 (49)	57.5 (2.6)	137.5 (6.3)	302.8 (33.5)
			II	0.399 (0.060)	21 (0.5)	213.8 (2.8)	34.8 (1.3)	1725 (38)	52.9 (1.8)	103.4 (9.5)	198.4 (6.5)
S22	N08°55.867' E038°45.428'	2174	I	0.460 (0.028)	51.8 (1.1)	272.3 (10.6)	54.6 (4.9)	1930 (44)	88.1 (2.1)	190.4 (23.0)	227.3 (7.8)
			II	0.419 (0.051)	26.2 (0.9)	252.6 (4.3)	45.3 (1.7)	1805 (54)	75.5 (2.9)	208.7 (17.0)	178.6 (8.9)
S23	N08°51.873' E038°44.394'	2069	I	0.493 (0.025)	29.5 (1)	247.0 (9.9)	51.9 (2.5)	1636 (49)	76.8 (2.7)	138.0 (7.6)	289.3 (25.6)
			II	0.420 (0.061)	29.1 (2.2)	204 (33)	44.3 (3.2)	1741 (132)	60.9 (6.1)	118.6 (9.0)	236.5 (19.4)

Conclusion

Methods have been developed for multi-element analysis of sediment samples. The microwave digestion process selected presents considerable advantages, which include good precision and accuracy, reduced contamination, speed and safety. The use of $\text{HNO}_3/\text{HCl}/\text{HF}/\text{H}_3\text{BO}_3$ acid mixtures allow the complete dissolution and thus the determination of the total contents of several analytes present in sediments without recovery problems.

The multi-element analysis capability of ICP-MS with high sensitivity, speed, high sample throughput and reliability of the technique coupled with microwave-assisted treatment of matrices makes the developed procedure very convenient for the analysis of sediment samples.

The present findings highlight that the heavy metal pollution state of TAR and some of its tributaries is alarming. This is due to the fact that in addition to the dumping of solid wastes the untreated wastewater from domestic, municipal and industrial sources constitutes the main sources of metals to the TAR and its tributaries (14). The installation of a water treatment plant is therefore a must in order to reduce the contamination loads, to preserve the living resources of the river and to avoid spread of heavy and trace elements with potential health hazards.

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