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A three-step metal fractionation scheme for fly ashes collected in an Argentine thermal power plant

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Abstract. A new three-step fractionation scheme was applied to study the distribution of Al, As, Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, S, Sb, Ti, V and Zn in fly ashes collected in the electrostatic precipitator of a thermal power plant in the city of San Nicolás (Argentina). Seven samples were collected during one week of operation in 2005. For the fractionation, the scheme applied consisted of extracting the elements in three fractions: (i) soluble and exchangeable elements, (ii) carbonates, oxides and reducible elements and (iii) residual elements. Metals and metalloids at μg g^{-1} level were determined in each fraction by plasma based techniques namely, inductively coupled plasma optical emission spectrometry (ICP OES) and inductively coupled plasma mass spectrometry (ICP-MS). For validation, a certified reference materials NIST SRM 2711 (Montana soil) was

subject to the same chemical sequential extraction procedure. X-ray diffraction powder (XRD) analysis and scanning electron microscopy (SEM) were used to characterize the major minerals present in the matrix. The predominant phases found in the total samples were mullite, quartz, iron oxides and lime. Total analyte concentration varied (in μg g^{-1}) from 1.54 for Cd to 30600 for Al. The leachability of the 15 elements under study proved to be different. All the elements (except Cd and Pb) were detected in the soluble fraction in the order: Cu (0.10%) ~ Mn (0.13%) < Ni (0.17%) ~ Ti (0.19%) ~ Fe (0.20%) ~ As (0.21%) < Zn (0.86%) < Al (1.3%) < Cr (2.9%) < V (3.9%) < Sb (6.9%) < Mo (45.1%) < S (58.0%). Percentages higher than 20% of S (24.1%) < V (27.5%) < Mn (29.0%) were detected in the second fraction. Al, As, Cr, Cd, Cu, Fe, Ni, Pb, Sb and Zn were mostly associated to the residual fraction. Recoveries of the overall procedure varied between 106% (Mo) and 72% (Cr).

Keywords: Coal fly ashes;; three-step fractionation scheme; trace elements; plasma-based techniques

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1. Introduction

Coal combustion is recognized as one of the major anthropogenic sources of many metals and metalloids into the atmosphere [1]. As an example, a 1000 MW power plant has a typical consumption of 12 000 t day^{-1} of coal [2] generating significant amounts of by-products. The amount and nature of metals and metalloids released are related to the composition of the coal burned and the technology employed at the power station. Coal contains many elements (As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Se, Sn,

etc.) and many of them have been reported to be human potentially carcinogens [3]. Electrostatic precipitators can remove more than 95% of the fly ashes but particles with aerodynamic diameters < 10 μm as well as any gaseous compounds will be emitted directly to the atmosphere. However, the possible fate of the different elements released during the combustion process requires proper understanding because those elements present on the surface of fly ashes particles will be mobile in the aqueous environment possibly representing a serious health risk.

The availability and mobility of elements present in fly ashes will depend on the physicochemical forms of the elements [4]. In this context, the knowledge of the chemical composition, physical characteristics and fractionation of the ashes are of prime importance to assess the environmental impact and health risks.

Chemical sequential extractions provide useful information about solubility, origin, mode of occurrence, biological and physicochemical availability, mobilization, fate and transport of trace metals in the environment [5]. These procedures are operationally defined. Their operationally defined nature may be considered a weakness. In spite of this, sequential extraction methods provide knowledge that can improve our understanding of the risks for human health and the environment. Recently, Smichowski et al [5] have reviewed metal fractionation of atmospheric aerosols, via sequential chemical extraction procedures. The same authors also reviewed the role of atomic spectrometric techniques in the determination of chemical elements in atmospheric aerosol, including fractionation studies [6].

Extraction methods have been developed and applied to chemical fractionation of fly ashes both for research and regulatory. Bódog et al [7] reported a five-stage leaching procedure applied to fly ash samples collected at several emission sources in Europe. The analysis of the extracts by atomic absorption spectrometry

(AAS) and graphite furnace atomic absorption spectrometry (GFAAS) showed different leachabilities and distribution patterns of Cd Cr, Cu, Pb, V and Zn. Smeda and Zyrnicki [8] used a modified BCR extraction scheme [9] for studying the distribution of metals in fly ashes.

Recently, Gómez and coworkers [10] reported a four-step fractionation scheme for metals and metalloids by chemical bonding for particles accumulated by electrostatic precipitation in a thermal power plant. This fractionation procedure was based on a sequential extraction scheme reported by Fernández et al [11] that was optimized for the analysis of fine atmospheric aerosols.

Continuous exposure to airborne particulate matter and fly ashes can have harmful effects on human health and the environment. In this context, a new three-step scheme was specifically adapted for the extraction of the more bioavailable elements present in fly ashes. Our previous studies applied to the fractionation of urban airborne particulate matter samples and fly ashes [10-14] demonstrated that the first two fractions contained the most bioavailable elements. Therefore, the third fraction constituted by metals bound to organic matter and sulphides was combined with the residual fraction. Commonly, very low proportion of trace elements are bound to the oxidizable fraction in pulverized coal combustor (PCC) fly ash because this fraction refers only to unburned coal particles and no sulphide species occur in combustion of coal. Summarizing, the new scheme is constituted by two fractions of elements with different mobility plus the last fraction, which unifies practically all non-bioavailable elements.

In the present study, the fractionation of ashes by chemical bonding was performed using a three-step chemical sequential leaching scheme focused to gain information on the most mobile fractions. It was carried out by assessing the distribution of 15 elements in seven samples, between i) soluble and exchangeable elements, ii)

elements bound to carbonates, oxides and sulphides (reducible elements), iii) environmentally immobile elements .

2. Experimental

2.1. Instrumentation and reagents

A Fisons-ARL (Accuris, Switzerland) sequential ICP OES Model 3410 inductively coupled plasma optical emission spectrometer was employed for major and minor element determination. Instrumental details and operating conditions are summarized in Table 1.

An Agilent Technologies (Santa Clara, CA, USA) inductively coupled plasma quadrupole mass spectrometer (ICP-QMS) Model 7500ce was used for trace elements determination. This instrument has an Octopole Reaction System (ORS) for elimination of polyatomic interferences arising from the plasma and sample matrix. Instrumental details and operating conditions are summarized in Table 2.

Welding Ar from Air Liquide (Paris, France) was used for ICP OES and ICP-MS determinations. Deionized distilled water (DDW) of Milli-Q grade was from Waters-Millipore (Billerica, MA, USA). All reagents were of analytical grade. Hydrochloric, hydrofluoric and nitric acids, and hydroxylamine chloride (Merck, Darmstadt, Germany) were used for sample treatment and preparation of the standards. Commercially available 1000 mg l^{-1} standard solutions for ICP determinations (Merck) of the elements analyzed were used. All glassware and Teflon® vessels were treated in a solution 10% v/v nitric

acid for 24 h and then washed with deionized water. All treated samples were stored in polyethylene tubes of 15 ml (Sterilin®).

A MLS-model Ethos 900 (Milestone-FKW, Sorisole, Bergamo, Italy) microwave apparatus equipped with six Teflon-PFA (perfluoroalkoxy) vessels was used to digest the samples.

X-ray powder diffraction patterns were taken at room temperature using a Philips PW 3710 diffractometer with Cu graphite monochromatized radiation. X-ray measurements were performed using the step mode using 0.02° per step with a 2 second counting time per step, over the range $10^{o} \leq 2\theta \leq 70^{o}$. For phase identification, the diffraction patterns obtained were analyzed using PC-Identify and ICDD database.

Morphological and compositional identification was performed by Scanning Electron Microscopy (SEM), with a Philips 515 microscope (Philips Export B. V., Eindhoven, The Netherlands) equipped with an EDAX PV9100 probe (EDAX International Inc., Prairie, View, IL, USA). All spectra were obtained at 20 kV in a 50-second analysis time.

2.2. Fly ash sampling

About 5 kg of fly ash samples were manually collected for seven consecutive days at different places from the electrostatic precipitators prior to being sent to the ash hoppers of a power plant located in Buenos Aires province, Argentina. This 650 MW power plant is the only one in Argentina that burns coal. This coal is normally imported from Australia, Colombia, or South Africa. During the sampling period the boilers used the same type of imported bituminous coal from South Africa (Gondwana type), producing as a residue, class-F fly ash.

Each of the seven as-received fly ashes was thoroughly homogenized using a v-blender (Patterson-Kelley Co., USA). The blended ashes were placed in clean polyethylene bags during transport to the laboratory and were stored in a dark and dry place.

2.3. Microwave assisted digestion for whole sample

Portions of 0.5 g of each sample were introduced into Teflon® vessels and subjected to microwave-assisted digestion using 15 ml of a mixture of HNO_3, HCl and HF (1:3:1). The digestion cycle adopted is detailed in Table 3. After acid digestion, 250 mg of boric acid was added in order to remove any residual HF.

Two portions were weighted for each sample. For quality control purposes, aliquots of a certified reference material from NIST (USA) SRM 2711 (Montana soil) was subject to the same treatment and included in the over-all analytical process.

2.4. Chemical sequential extraction for element fractionation in coal fly ashes

Samples were simultaneously subject to a three-step leaching procedure and the following fractions were obtained:

Fraction 1: about 500 mg of each of the seven solid samples were carefully weighed, placed in 50 ml Falcon® tube and 15 ml of ultra pure water, adjusted to pH 7.4 by adding NH_4OH,. Continuous agitation at room temperature in a mechanical shaker at 50±5 rpm was maintained for three hours according to our previous studies [14, 15]. The samples were then centrifuged for three minutes at 5000 rpm. Aliquot of between 10 and 13 ml of the supernatant was carefully taken with a micropipette and placed in a clean 15 ml

Sterilin® tube of (Fraction 1). The rest of the supernatant was discarded and the solid residue was used for the next extraction.

Fraction 2: 15 ml of 0.25 mol l^{-1} hydroxylamine chloride acidified at pH 2 with HCl were added to the solid residues of Fraction 1. Falcon® tubes were closed and continuous agitation at room temperature in a mechanical shaker at 50±5 rpm was maintained for five hours. The samples were then centrifuged for three minutes at 5000 rpm. An aliquot between 10 and 13 ml of the supernatant was carefully taken with a micropipette and placed in a clean 15 ml Sterilin® tube of (Fraction 2). All the residues were carefully transferred to a microweable Teflon® vessel.

Fraction 3: 15 ml of a 1:3:1 mixture of 65% HNO_3, 37% HCl and 40% HF were added to the solid residue of Fraction 2. The microwave oven was operated according to the same program that was used for total elements determination (Table 3). After cooling, about 250 mg of boric acid were added to remove any residual HF. An aliquot between 10 and 13 ml of the supernatant was carefully taken with a micropipette and placed in a clean 15 ml Sterilin® tube (Fraction 3). The fractionation procedure adopted is summarized in Table 4.

The same three-step chemical extraction procedure was performed without a sample and the blank values thus obtained (reagents + tubes) were subtracted from the ICP OES/ICP-MS measurements of the determined elements.

2.5. Sample analysis

Inductively coupled plasma-based techniques namely, ICP OES and ICP-MS were employed for the determination of metals and metalloids in the fly ash samples. These techniques can be applied to different matrices once a suitable dissolution procedure has

been established. They typically exhibit extended dynamic concentration ranges (4-6 orders of magnitude), are multielemental in nature and possess high sensitivity and appropriate detection power.

Specifically, Al, As, Fe, Cd, Cr, Cu, Mn, Mo, Ni, Pb, S, Sb. Ti, V and Zn in the whole sample and residual fractions were determined by ICP OES. The same elements, except Al and Fe, were quantified by ICP-MS in the two first fractions of the fractionation scheme.

Experiments showed that when standard addition calibration graphs for the extracts of fly ashes were compared with direct calibration graphs obtained with calibrants prepared in the corresponding extractant solution no significant differences were observed. For this reason, three sets of multi-elemental calibrants for ICP OES determinations were prepared to analyze each fraction. The calibrants were prepared from 1000 μg l^{-1} standard solutions of the individual elements in the same matrix as the fraction. All measurements were performed by triplicate and the reported results are averaged values.

Inductively coupled plasma quadrupole mass spectrometry was used for elemental quantification. The formation of spectral interferences originating from atomic and molecular ions produced in the Ar plasma by the matrix constituents of the samples affects the quantification of several trace elements. For those elements that exhibited this kind of interferences (e.g. As and V) and depending on the their concentration, we used the ICP-MS with the reaction cell or we used mathematical equations for interference correction.

3. Results and discussion

3.1. Characterization of bulk fly ashes by XRPD, SEM and EDAX

Fly ash from coal combustion is a complex and heterogeneous material**.** As a consequence of the rapid heating and cooling the composition and morphology of mineral matter derived from the coal may undergo different effects such as oxidation, decomposition, disintegration or agglomeration [16]. All these processes result in the formation of amorphous phases, spherical particles, agglomerates and hollow cenospheres. Morphological characterization by SEM of the seven fly ashes samples is shown in Figure 1. In general, the typical fly ashes particles could be observed, porous and irregular shapes, fine solid and hollow spheres, presence of char due to an incomplete combustion of coal and molten glassy materials. All the samples were analysed by EDAX for elemental determination. Similar composition was found for fly ash particles. Those are made up of Al, Ca, Cl, Fe, Mg, Na, S, Si and Ti.

All the samples revealed a similar diffraction pattern, with dominant silicate mineral abundance, mineral oxides and high amorphous occurrence as it is shown in Figure 2. The mineral and chemical composition shows that the major minerals are quartz (SiO_2) and mullite ($Al_6Si_2O_{13}$) confirming that the coal burned in the power plant produces class-F fly ash. The other mineral phases present as minor or accessory are lime, anhydrite, hematite, magnetite, gypsum and rutile.

3.2. Quality parameters

Detection limits were calculated following the IUPAC rules on the basis of 3σ-criterion for ten replicate measurements of the blank signal. Limits of detection achieved for Al, As, Cd, Cr, Cu, Fe, Mn, Mo, Ni, Pb, S, Sb, Ti, V and Zn are listed in Table 5. The relative

standard deviations (RSDs) for 13 of the 15 elements evaluated are in general in a more than satisfactory interval (0.4 to 11.4 %) considering the complexity of the matrix analysed and the considerable number of manipulations performed. Sulfur (11.4%) and As (8,2%) exhibited higher RSDs (Table 6).Comparison between total concentrations obtained applying the procedure adopted and the subsequent sum of the individual concentrations in the fractions is a possible alternative to check for possible systematic errors arising from element losses, contamination or other undefined causes. In this context, a Standard Reference Material namely NIST 2711 (Montana soil) was subject to the same sequential extraction scheme as the fly ash samples. For the determination of total metal concentrations, the SRM was digested using the same acid mixture employed to dissolve the residual fraction. Table 6 summarizes data on total concentration of the analytes in the digested SRM and the results of the sum of the individual fractions as determined by ICP OES or ICP-MS as well as the certified values. Results of the SRM analysis (Table 6) show that the elements that exhibited good recoveries were: Cd, Sb and V (96-97%); Ni and Ti (105%); Mn (92%) and S and As (110%). According to the intervals of recovery recommended by the A.O.A.C., the major elements Al (109%) and Fe (89%) and the trace elements Cu (123%), Zn (78%) and Pb (66%) had recovery values outside the corresponding interval. Despite this, their standard deviations were low (0.03-1.4), except for Pb (29). Therefore, the high reproducibility indicates that the recoveries can be considered acceptable for this complex matrix.

3.3. Bulk concentrations of metals and metalloids

Bulk analyte concentrations of the seven acid-digested fly ash samples varied from 1.5 for Cd to ~ 31000 μg g^{-1} for Al (Table 7). Major components include quartz

(SiO_2), mullite (SiO_2-Al_2O_3), Fe oxides (Fe_2O_3), metallic Fe (Fe^o), Ti oxide (TiO_2) and sulfates ($SO_4^=$).

Aluminum > Fe > Ti > S > V were the major components in all the samples. Minor elements were: Mn > Ni > Cr. The remaining elements were found at trace levels: Cu > As > Zn > Pb > Mo > Sb > Cd. Minimum and maximum bulk concentrations found in individual samples (expressed in μg g^{-1}) were Al, 27676-35791; Fe, 7466-8487; Ti, 2721-2965; S, 1238-1394; V, 1087-1156; Mn, 268-277; Ni, 231-245; Cr, 137-142; Cu, 78.8-80.9; As, 63.1-98.4; Zn, 52.1-59.2; Pb, 24.2-34.1; Mo, 6.98-8.42; Sb, <1.50-4.73; and Cd, 0.96-2.19.

3.4. Metal fractionation and efficiency of fractionation

The twenty-one sub-samples obtained by sequentially extracting the three fractions from each of the seven ash samples studied were analyzed simultaneously to determine the concentration of 15 elements. Variations of element concentrations per fraction between the corresponding seven ash samples were assessed by means of the coefficient of divergence (COD) as defined in eqn. 1 [17]. In this case, $COD_{f,jk}$ represents the coefficient of divergence of fraction f (f=1,3 with f=4 representing the bulk sample), $x_{f,ij}$ stands for the measured concentration in fraction f (μg g^{-1}) of a chemical component i in ash sample j; and j and k represent two different samples (j=1,7 and k=1,7). The COD is self-normalizing; if two samples are similar in chemical composition the COD approaches zero, otherwise the COD approaches one.

$$COD_{f,jk} = \sqrt{\frac{1}{15}\sum_{i=1}^{15}\left(\frac{x_{f,ij} - x_{f,ik}}{x_{f,ij} + x_{f,ik}}\right)^2} \qquad \text{(Eqn. 1)}$$

For each fraction, we calculated 21 CODs representing all possible combinations between the seven ash samples. As indicated in Table 7, the seven bulk ash samples are very similar in trace element concentrations; this fact is corroborated with the low average value of COD_4 (0.12±0.03). With respect to the extracted fractions, the soluble fraction (f=1) with average COD_1 of 0.31±0.11 exhibited the largest variations, the reducible group (f=2) with average COD_2 of 0.19±0.09 presented an intermediate degree of similarity while the concentrations in the residual fraction (f=3) with average COD_3 of 0.14±0.03 showed a more homogenous pattern similar to that of the bulk ash. The largest differences in the soluble fraction are associated with Cu > Ti > Mn = Ni. Each of these elements presented in the seven sub-samples of Fraction 1 large differences in very low concentrations that in average represent less than 0.2% of the concentration of the bulk ash. For the elements that are present at higher concentrations the differences in concentrations are lower. An overview of the CODs values thus indicate that the concentrations are rather similar in the seven sub-samples and that the variations are most likely associated with minor variations in coal composition during the seven-days sampling period.

On the basis of the similar concentration profiles observed for all the ash samples analyzed, the average of the sum of the fractional concentrations were calculated and in this way the measured concentrations are summarized in Fig. 3.

The fractionation scheme divided the total metal concentration in three partial concentrations; consequently, the sum of the three partial values of concentration should

coincide with total metal concentration. The comparison between this sum and the total metal concentration provides the performance of the extraction scheme. The control of the efficiency in the fractionation procedure was defined in terms of the recovery, as follows in Eqn. 2.

$$\text{Recovery} = 100 \times \frac{\sum_{j=1}^{7}\left(\sum_{i=1}^{3}\left(\text{Fractional concentration}\right)_i\right)_j}{\sum_{j=1}^{7}\left(\text{Average total concentration}\right)_j} \qquad \text{(Eqn. 2)}$$

where, i = 1 to 3, represents the fraction number and j = 1 to 7 stands for the number of fly ash sample. Fig. 3 provides an overall picture of the concentrations of 15 elements after MW-assisted digestion and the sum of fractions. All the recoveries were found to be good or acceptable considering the complexity of the matrix analyzed and the number of manipulations performed. Recoveries varied in the order Mo (106%) > Pb (100%) > As (98%) > Ti (96%) > Zn (93%) > Cu ~ Al (89%) > Mn (88%) > S (87%) > Fe (85%) > V (83%) > Sb (79%) > Cd (76%) > Ni (74%) > Cr (72%).

Results of elements distribution among the three fractions (Fig. 4) evidenced that the majority of elements were found in the residual fraction (Fraction 3), except Mo and S with percentages of 41% and 18% respectively). Only Mo (45%) and S (58%) exhibited appreciable percentages in Fraction 1 with Sb present to a lesser extent (~ 7%). The high content of soluble S is consistent with the physico-chemical characterization that reported that S was present as sulfate compounds ($MgSO_4$ and $CaSO_4$-Gypsum). At the combustion temperature of this power plant, volatile elements such as Mo vaporize in the combustion zone and condense on particles when flue gas leaves the combustion zone and become enriched on the surface of fly ash particles [2]. This fact may help to explain the high concentration of Mo in Fraction 1, considering that the solubility of surface enriched elements is controlled by dissolution and surface sorption and complexation

processes [18]. In solubility studies on size-segregated coal fly ashes reported by Seames et al. [19], the authors observed that Sb was very soluble at pH 2.9 and fairly soluble at pH 5. Their results were consistent with the following compounds, Sb, Sb_2O_4, and Sb_2O_5 but inconsistent with Sb_2O_3.

A ~ 4% of V was found in the soluble fraction. This element is likely to be present in the ash as vanadate. These results are in good agreement to those reported by Font and coworkers [20]

With regard to contributions in the reducible group (Fraction 2), Mn (29%), V (28%) and S (24%) were those that presented the highest values. Other elements with lesser percentages in Fraction 2 were As, Mo and Sb with values around 13-14%.

As the soluble fractions are of most environmental concern, they were studied in greater detail. Fig. 5 represents the percentages of the first two fractions (normalized exclusively to the sum of them). In this case, besides S (71%) and Mo (76%), Al (85%) was the element with the highest percentages in the soluble fraction (Fraction 1), predominating over Fraction 2. The rest of elements presented higher percentages in the second fraction than in the soluble one, except Cr and Ti, with similar contributions in both fractions. According to Vassilev et al [21] Ti may be present as oxyhydroxide in Fraction 1, whilst TiO_2 was the Ti oxide present in Fraction 2. The elements with higher percentages in Fraction 2 were As, Cd, Cu, Mn, Ni, Pb, V and Zn with values close to 100%. Fe (75%) and Sb (66%) were the other elements with recoveries higher than 50% found in Fraction 2. Fe_2O_3 was probably the Fe compound present in Fraction 2, whilst Zn could be present as oxide (ZnO). The rest of elements in Fraction 2 could be present also as oxides. Calcium is present, according to the physico-chemical analysis, as sulfate compounds in the soluble phase, as well as oxide in the total phase.

4. Conclusions

A three-step chemical sequential extraction procedure has been applied to fly ash samples collected in the electrostatic precipitator of a thermal power plant. This study further supports the contention that the knowledge of the levels of toxic and potentially toxic elements, especially in the most mobile fractions, is an important tool for environmental risk assessment. This scheme demonstrated to be efficient with recoveries ranged from 72 % (Cr) to 106 % (Mo). For total concentrations good recoveries were obtained regarding the AOAC intervals.

The elemental concentration of the bulk fly ash from the South African coal is within the range of bituminous coals with the exception of Ni and V that are higher than the values indicated in the literature. This may be associated with the sporadic use of residual fuel oil in this power plant.

The leachability of the 15 elements under study proved to be different for most elements. Sulphur and Mo were found to be the most abundant elements in the water phase (54-62%) followed by Sb (~ 7%) > V (~ 4%) > Cr (~ 3%) > Al~Zn (~ 1%). For the other elements studied the leachable fraction was in all cases < 0.2% of the bulk content. Al, Cd, Cu, Cr, Fe, Pb, Ni and Ti were mostly associated with the residual fraction (> 90%).

Considering the high mullite content of the studied fly ash, potential applications are the production of ceramic or refractory materials.

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Table 1

Instrumental characteristics and settings for ICP OES

Instrument	A Fisons-ARL sequential ICP-OES, Model 3410 Forward Rf power 650 W
Frequency of rf generator	27.12 MHz
Coolant gas flow rate	7.5 l min^{-1}
Auxiliary gas flow rate	0.8 l min^{-1}
Sample gas flow rate	0.8 l min^{-1}
Solution delivery	2.3 ml min^{-1}
Nebulizer	Concentric of glass, Meinhard type
Polycrhomator	Photomultiplicator R955-1, focal distance 100 mm to 546.07 nm, crack 2400 lines mm^{-1}
Torch	Axial view
Measurement mode	Continuous nebulization
Wavelengths (nm)	Al, 396.152; As, 193.759; Cd, 226.502; Cr, 267.716; Cu, 324.754; Fe, 259.940; Mn, 257.610; Ni, 231.604; Pb, 220.353; S, 180.731; Sb, 206.833; Ti, 334.941; V, 292.402; Zn, 213.856; Mo, 202.030

Table 2

Instrumental characteristics and working conditions for the determination of trace elements in fly ashes by ICP-MS.

Spectrometer	Agilent Technologies, Model 7500c
Reaction cell	Octopole Reaction System (ORS)
Rf power	1500 kW
Nebulizer	Pneumatic, Babington type
Interface	Sampler and skimmer cones in Ni
Data acquisition	Spectrum; 3 passes
Argon flows (l min^{-1})	Plasma, 14.9; auxiliary, 0.9; carrier gas, 1.22; makeup 0.0
Analytical masses (amu)	^{27}Al, ^{56}Fe, ^{32}S, ^{75}As, ^{106}Cd, ^{108}Cd; ^{111}Cd, ^{114}Cd, ^{52}Cr, ^{53}Cr, ^{54}Cr, ^{63}Cu, ^{65}Cu, ^{55}Mn, ^{60}Ni, ^{62}Ni, ^{206}Pb, ^{207}Pb, ^{208}Pb, ^{121}Sb, ^{123}Sb, ^{46}Ti, ^{47}Ti, ^{51}V, ^{95}Mo, ^{97}Mo, ^{98}Mo, ^{66}Zn, ^{67}Zn, ^{68}Zn
Internal standard mass (amu)	^{103}Rh

Table 3

Working conditions for the MW digestion of fly ashes.

Reagents	15 ml of a mixture of HNO_3, HCl and HF (1:3:1).	
Digestion cycle		
Step	MW power (W)	Time (min)
1	300	10
2	0	1
3	600	5
4	0	4 (cooling stage)

Table 4

Chemical fractionation scheme of elements applied to the fly ashes collected in the electrostatic precipitator

Fraction	Reagent	Experimental conditions
(i) Soluble and exchangeable elements	15 ml H_2O (pH 7.4)	3 h at room temperature. Shaker agitation
(ii) Carbonates, oxides, reducible elements	15 ml NH_2OH•ClH 0.25 M at pH 2	5 h at room temperature. Shaker agitation
(iii) Residual elements	10 ml HNO_3**:**HCl**:**HF (2:6:2) + boric acid	20 min at MW oven

Table 5

Limits of detection (LOD) achievable for fly ashes by ICP OES or ICP-QMS

Element	ICP OES LODs (3σ) in fly ashes ($\mu g\ g^{-1}$)	ICP-QMS LODs (3σ) in fly ashes ($\mu g\ g^{-1}$)
Al	2.0	0.8
As	6.5	$6\ 10^{-3}$
Cd	0.86	$9\ 10^{-3}$
Cr	1.6	$1\ 10^{-6}$
Cu	2.7	$9\ 10^{-3}$
Fe	1.1	$5\ 10^{-4}$
Mn	1.8	$6\ 10^{-7}$
Mo	5.1	$6\ 10^{-4}$
Ni	2.1	$6\ 10^{-3}$
Pb	3.0	$2\ 10^{-8}$
S	3.5	$6\ 10^{-3}$
Sb	1.6	$2\ 10^{-3}$
Ti	2.1	$1\ 10^{-7}$
V	5.1	$3\ 10^{-2}$
Zn	3.7	$2\ 10^{-6}$

Table 6

Recoveries obtained in analysis of the SRM NIST 2711 (Montana soil). *Rec1* is the recovery regarding the Certified value (C). *Rec2* is the recovery of the sum of fractions (S) with regard to the experimental total concentration (T). Cr and Mo are the non-certified elements

Elements*	Certified(C)	SD	RSD(%)	Total(T)	SD	RSD(%)	Sum(S)	SD	RSD(%)	Rec1(T/C)	Rec2(S/T)
Al	6.53	0.09	1.4	7.13	0.28	3.9	6.75	0.32	4.7	109.	94.7
As	105	8	7.6	115	9	8.2	107	6	5.3	110	92.8
Cd	41.70	0.25	0.6	40.5	0.17	0.4	40.2	0.49	1.2	97.0	99.5
Cu	114	2	1.8	140	1	0.4	150	5	3.4	123	107
Fe	2.89	0.06	2.1	2.58	0.03	1.2	2.82	0.05	1.9	89.3	109
Mn	638	28	4.4	590	3	0.6	587	15	2.6	92.4	99.5
Ni	20.6	1.1	5.3	21.9	0.9	3.9	22.9	15.5	67.7	106	105
Pb	1162	31	2.7	764	29	3.8	572	2	0.3	65.7	74.9
S	0.042	0.001	2.4	0.046	0.005	11.4	0.0480	0.0064	13.4	109	10
Sb	19.4	1.8	9.3	19.0	1.1	5.7	17.6	0.7	3.7	97.9	92.9
Ti	0.306	0.023	7.5	0.326	0.005	1.4	0.288	0.018	6.3	107	88.2
V	81.6	2.9	3.6	79.3	1.3	1.6	65.0	70.1	108	97.2	81.9
Zn	350.4	4.8	1.4	274	1.4	0.5	264	4.9	1.9	78.1	96.3
(Cr)	(47.0)			38.2	0.4	1.1	29.7	10.4	35.1	(81.2)	77.6
(Mo)	(1.6)			1.73	0.6	37.5	1.46	0.6	39.7	(108)	84.3

* All results are expressed in $\mu g\ g^{-1}$, except for Al, Fe, S and Ti that are expressed in percentage.

Table 7

Total metal concentration (in μg g^{-1}) of the seven acid-digested fly ash samples

Sample	Al	Fe	Ti	S	V	Mn	Ni	Cr	Cu	As	Zn	Pb	Mo	Sb	Cd
1	27676	8022	2803	1373	1144	276	235	142	80.3	65.6	55.7	28.0	7.67	2.33	1.68
2	29077	7466	2721	1323	1087	268	232	140	78.8	63.1	52.3	27.9	8.42	1.80	1.94
3	28336	7714	2795	1358	1095	274	231	137	79.4	72.0	52.1	32.3	6.99	2.33	2.19
4	30523	7844	2850	1394	1156	273	235	140	78.9	76.0	53.2	34.1	7.26	4.73	1.36
5	30443	7980	2898	1343	1124	269	238	139	80.3	84.5	55.2	24.2	7.54	0.89	1.18
6	35791	8119	2933	1238	1104	273	237	139	80.9	98.4	54.8	30.4	6.98	<1.5	0.96
7	32568	8487	2965	1298	1153	277	245	142	80.7	79.2	59.2	33.2	7.35	2.36	1.44
Mean	30631	7947	2852	1332	1123	273	236	140	79.9	77.0	54.6	30.0	7.46	2.06	1.54
SD	2794.1	322.6	85.9	52.2	28.5	3.4	4.6	2.0	0.9	12.0	2.5	3.5	0.5	1.5	0.4
RSD (%)	9.1	4.1	3.0	3.9	2.5	1.2	2.0	1.4	1.1	15.6	4.6	11.7	6.6	71.5	27.9

CAPTIONS OF THE FIGURES

Figure 1: SEM image of: a) general view of fly ashes, b) image of an aluminosilicate hollow sphere, c) irregular shape of amorphous phase, d) typical fly ashes spheres and e) vesicular aluminosilicate particule

Figure 2. Typical XRD pattern of the coal fly ashes. Mineral abbreviation: A-Anhydrite; H-Hematite; L-Lime; M-Mullite, R-Rutile; Q-Quartz

Figure 3. Comparison between the recoveries obtained after MW-assisted digestion of the bulk fly ash sample and the sum of the fractions obtained by the three-step extraction procedure.

Figure 4. Element distributions in fly ashes. Percentages regarding the sum of the fractions.

Figure 5. Element distributions in fly ashes. Percentages regarding the sum of Fraction 1 and Fraction 2, exclusively.

Figure 1

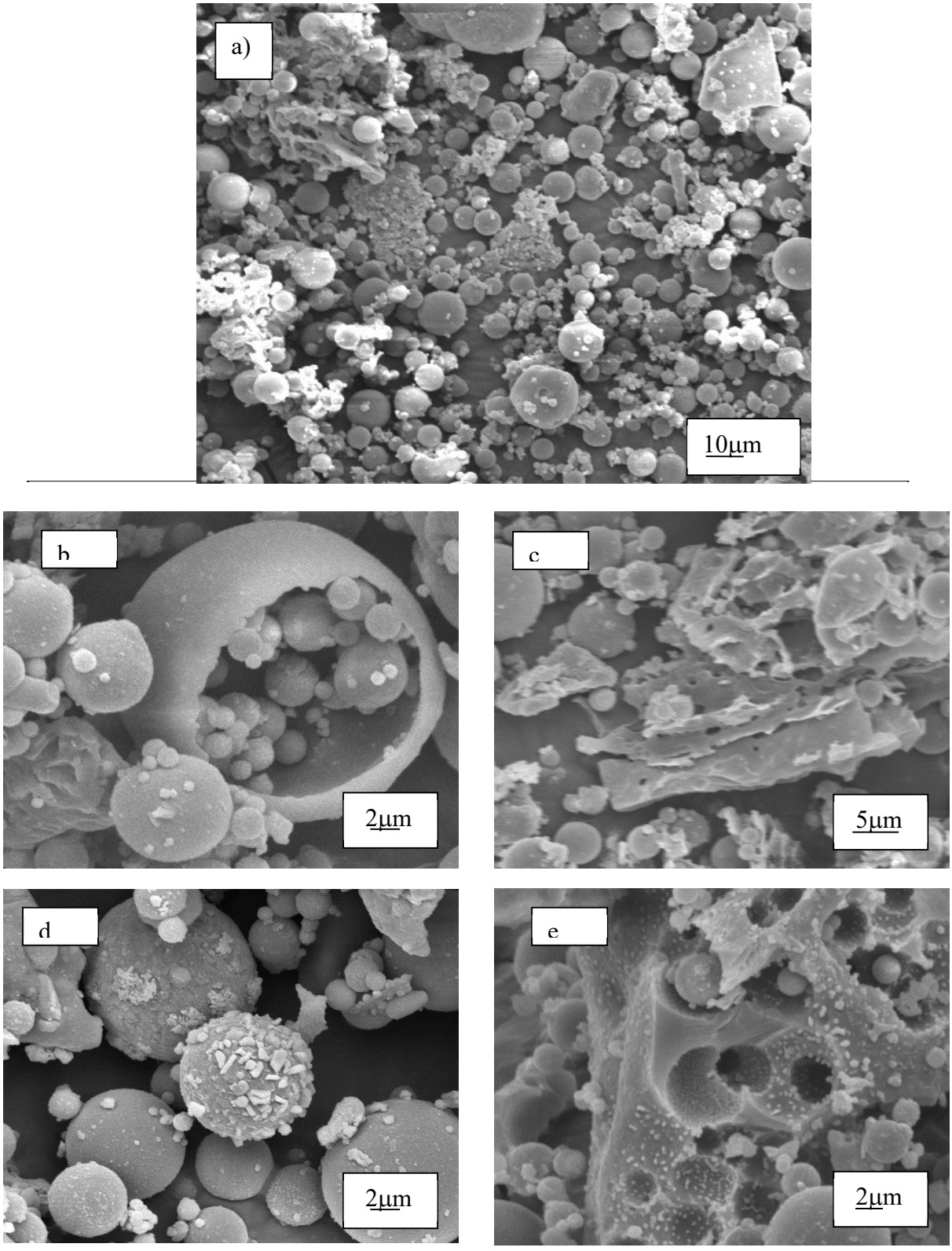
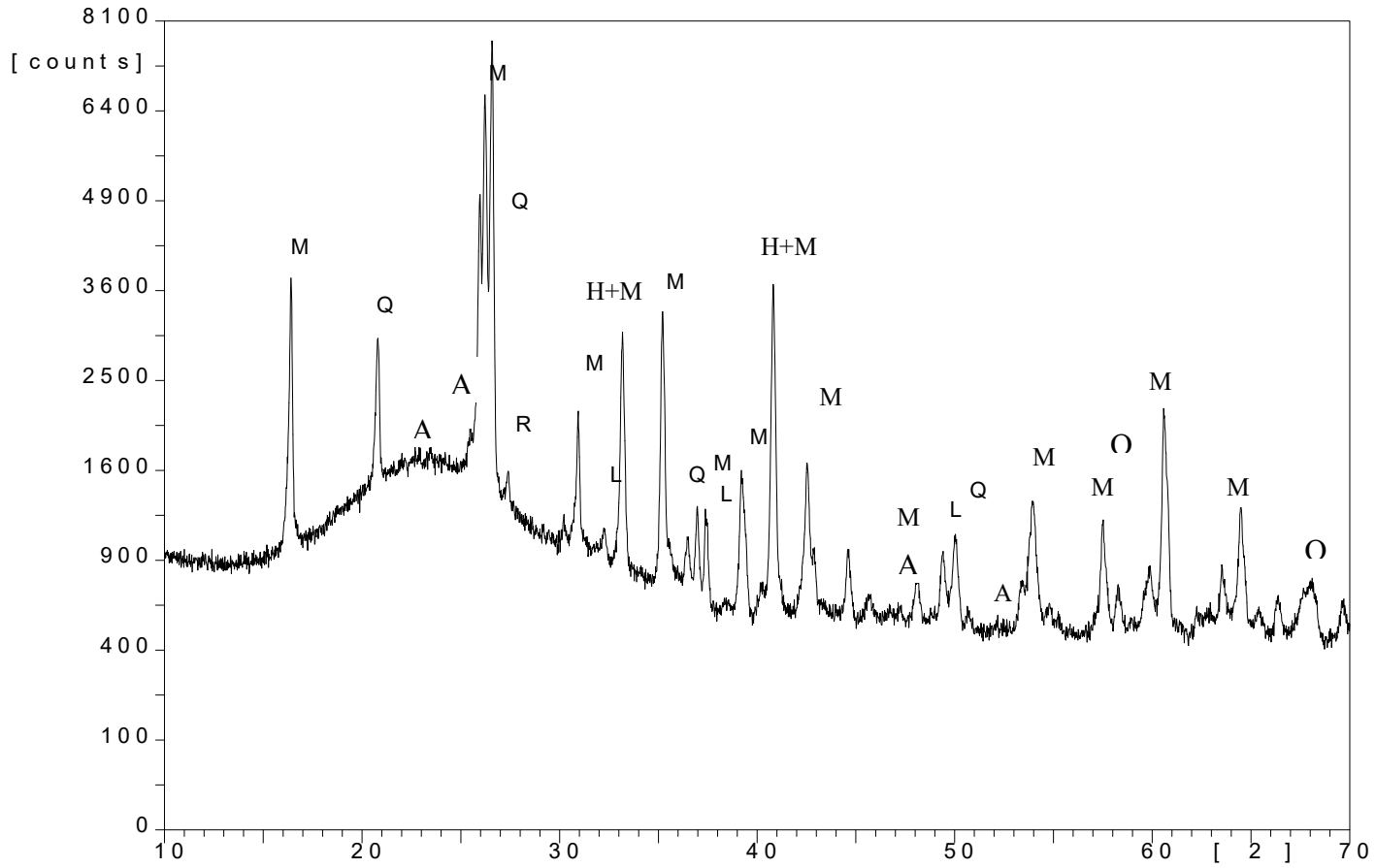


Figure 2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M
Q
A
R
H+M
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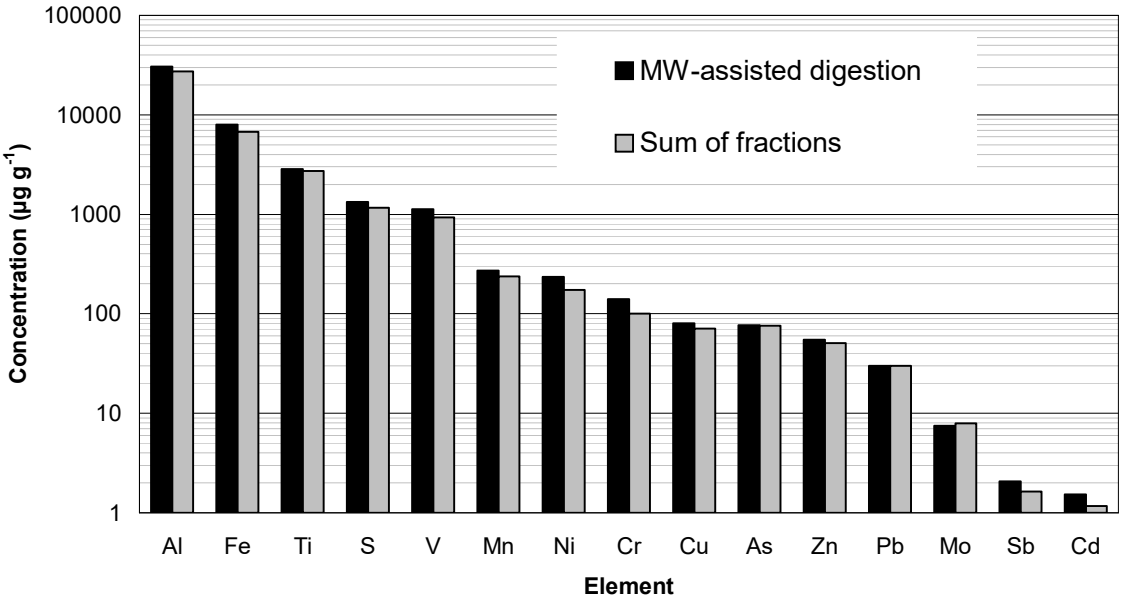
Figure 3.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Concentration (µg g-1)
MW-assisted digestion
Sum of fractions
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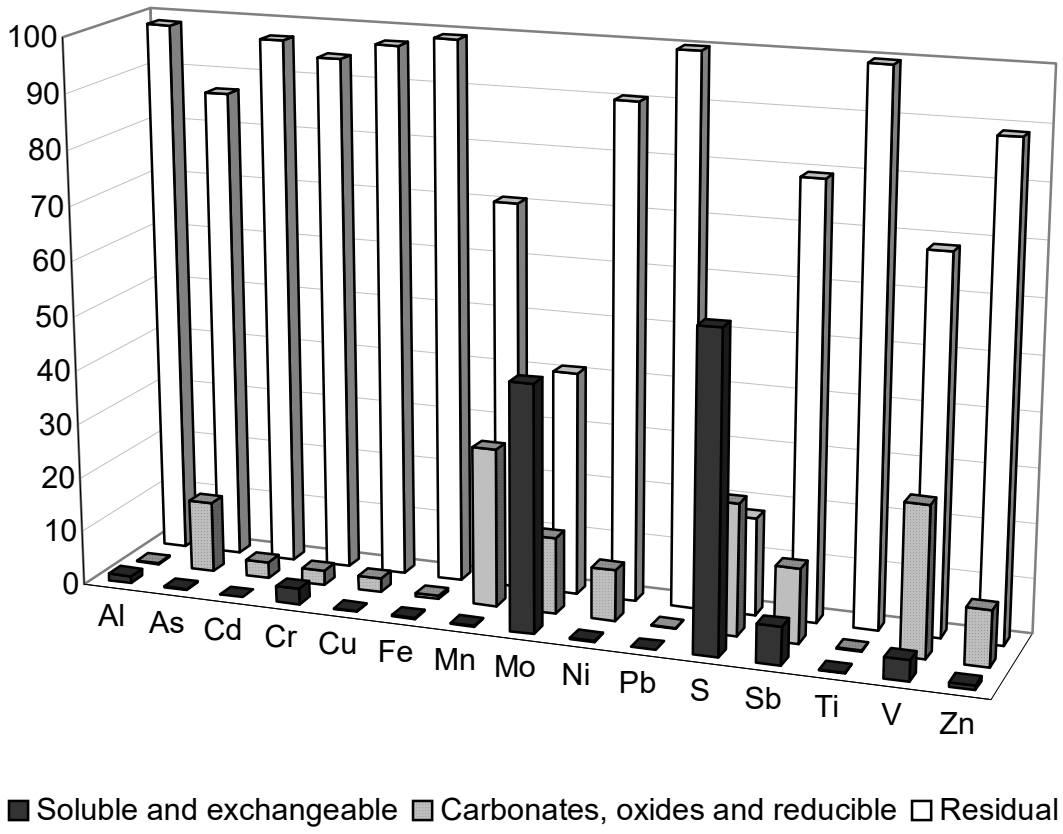
Ti
S
V
Mn
Ni
Cr
Cu
As
Zn
Pb
Mo
Sb
Cd
Element

Figure 4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Pb
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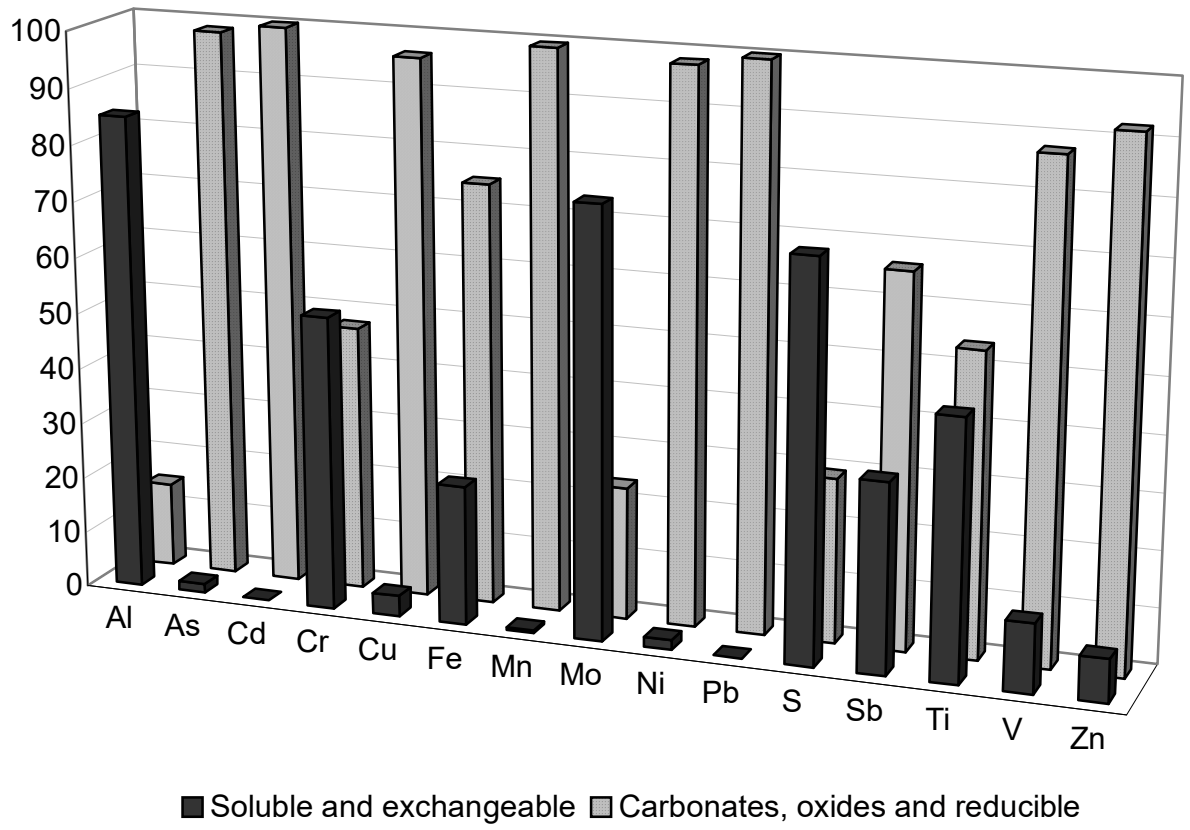
Sb
Ti
V
Zn
Soluble and exchangeable
Carbonates, oxides and reducible
Residual

Figure 5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Sb
Ti
V
Zn
Soluble and exchangeable
Carbonates, oxides and reducible