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Fractionation of trace elements in total atmospheric deposition by filtrating-bulk passive sampling

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ABSTRACT

We have developed and validated a new simple and effective methodology for fractionation of soluble and insoluble forms of trace elements in total atmospheric deposition. The proposed methodology is based on the modification of a standard total deposition passive sampler by integrating a quartz fiber filter that retains the insoluble material, allowing the soluble fraction to pass through and flow to a receiving bottle. The quartz filter containing the insoluble fraction and the liquid containing the soluble fraction are then separately assayed by standardized ICP–MS protocols. The proposed atmospheric elemental fractionation sampler (AEFS) was validated by analyzing a Coal Fly Ash reference material with proper recoveries, and tested for field fractionation of a set of 10 key trace elements in total atmospheric deposition at the industrial area of Puchuncaví–Ventanas, Chile. The AEFS was proven useful for pollution assessment and also to identify variability of the soluble and insoluble fractions of the selected elements within the study area, improving the analytical information attainable by standard passive samplers for total deposition without the need of using sophisticated and high cost wet-only/dry only collectors.

1. Introduction

Elemental profile is a key fingerprint for the chemical characterization of atmospheric deposition providing interesting data for the evaluation of its impact on human health and the environment, including the identification of specific emission sources [1]. Trace element analysis of atmospheric deposition is highly demanded for assessing air quality, health and environmental risks, and therefore a great deal of research has been focused on the metal composition of atmospheric suspended particulate matter. Most of the studies dealing with determination of trace metals in atmospheric deposition are focused on the determination of total metal concentration without distinguishing the various species that are present, but for risk assessment of metal toxicity, it is important to determine bio-accessible concentrations instead of total metal contents [2,3]. Furthermore, it is widely recognized that the study of elemental solubility provides useful information about the biological and environmental availability of specific elements contained in particulate matter. As a result, growing research interest is focused on novel, optimized procedures for extracting airborne elements, and for acquiring and interpreting data on their solubility. A range of single and multiple steps fractionation schemes have been developed to characterize different degrees of elemental solubility in atmospheric particulate matter, by utilizing water, solvents of varying acid strengths, and physiological media [3]. The fractionation schemes reported in the literature have been used to characterize pollution sources, to evaluate metal mobility and bioavailability, and to identify binding sites of metals in order to assess metal accumulation, pollution and transport mechanisms. Weak (aqueous) extraction procedure simulating particle dissolution close to neutral pH, such as in the human lung, can be used for toxicological purposes [4]. Water extraction is also representative for particle weathering after deposition, informing about bio-accessibility for soil organism and plants [5].

Several authors have explored extractability of airborne elemental species in water as an indication of bio-accesibility, as recently reviewed by Mukhtar and Limbeck [3]. The most common approach is active sampling of aerosols (PM10 and PM2.5) at the sampling site by aspiration of air through a filtering media. The sample is then transferred to the lab and treated with water by mechanical shaking [6,7], ultrasound energy [8], or microwave assisted heating [9]. Active air sampling is an expensive and sophisticated technique requiring a power source, a vacuum pump and a caudal meter, appropriate fitting and casing for outdoor use, making it inappropriate for unattended operation during

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experimental campaigns, especially at remote places. On the other hand, passive sampling has emerged as a tool for obtaining reliable analytical information in environmental quality monitoring [10]. Collection of atmospheric deposition by passive sampling can be performed by different experimental approaches, including a set of automatic dry-only, wet-only and water surface collectors, but the simplest mode is based on the so called atmospheric total deposition collectors (sometimes referred as bulk deposition collectors), offering distinct advantages through equipment simplification and ease of operation. The technique has been standardized by inclusion in the European norm EN 15841:2010 [11] for the determination of arsenic, cadmium, lead and nickel in atmospheric deposition as standard, and it is routinely incorporated in monitoring campaigns for atmospheric trace elements [12–14].

Trace element fractionation in atmospheric deposition collected by passive samplers has been attempted by some researchers. Morselli et al. [15] estimated soluble and insoluble fractions of heavy metals in wet and dry atmospheric depositions by a DDAS (dry deposition on aquatic surface) sampler. A similar approach was used by Muezzinoglu et al. [16] for the measurement of suspended and dissolved forms of selected heavy metals.

In the present study, we propose the new concept of fractionation of elements in atmospheric deposition by a passive atmospheric total deposition collector modified with a quartz fiber filter. This concept, designed as filtrating-bulk sampler, has been explored by some researchers for pH and major ions monitoring in the frame of acid rain investigations [17–19] but no reference has been found about its use for elemental fractionation. We propose this system and a simple and convenient analytical tool to obtain enriched chemical information from atmospheric deposition, allowing potential toxicity estimation with significant cost savings in atmospheric monitoring protocols.

2. Experimental

2.1. Reagents

All chemicals used for the preparation of stock and standard solutions were of analytical grade. Y(III) 1000 mg L^{-1} solution was supplied by Panreac (Barcelona, Spain). 1000 mg L^{-1} elemental standard solutions were supplied by Scharlau (Barcelona, Spain). Working solutions were prepared by dilution with ultrapure water obtained from a Wasserlab Ultramatic (Navarra de Tratamiento del Agua S.L., Pamplona, Spain) system. Reference materials and real samples were adjusted to pH 2 with sub-boiled HNO_3 obtained from a quartz sub-boiling system (Kürner, Rosenheim, Germany). 70% $HClO_4$ suprapur (Merck, Darmstadt, Germany) and 48% HF Hiperpur (Panreac, Barcelona, Spain) were used for sample treatments.

2.1.1. Reference materials and real samples

Certified Reference Material 1633c Coal Fly Ash (NIST, USA) was used for accuracy testing.

Weekly, atmospheric deposition samples were collected from several air quality monitoring stations in the vicinity of a copper smelter located at Puchuncaví, Chile. The Puchuncaví valley, a Mediterranean climate region placed in the coastal area of central Chile (71°24′S, 32°40′N), is characterized by marked pollution due to the discharge of gaseous pollutants and atmospheric particulates, and deposition of metal-rich particles from diverse industrial facilities including coal-fired power plants, a copper refinery and smelter, natural gas terminals and cement companies. A total of 14 samples were collected at the locations of La Greda (LG), Los Maitenes (LM), Puchuncaví (Pu) and Valle Alegre (VA) as shown in Fig. 1.

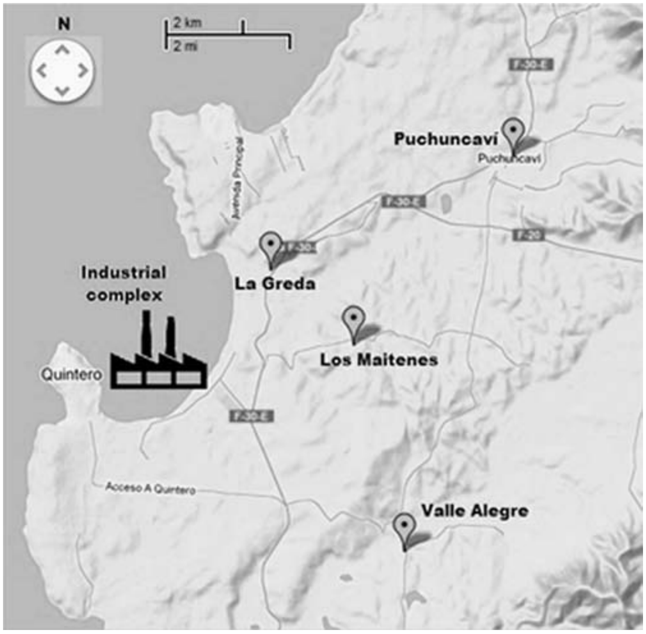

Fig. 1. Sampling locations of atmospheric deposition around the industrial complex of Puchuncaví–Ventanas, V Region, Chile.

2.2. Instrumentation

The AEFS devices we propose here for soluble and insoluble trace element fractionation in atmospheric deposition are derived from standard total atmospheric deposition polyethylene collectors (as described, e.g. in [11]). As depicted in Fig. 2, the proposed AEFS consists of: 1) an upper polyethylene bottle with a funnel end; 2) a polyethylene connection ring; 3) a perforated disk aimed to retain extraneous matter (insects, leaves, straws and the like); 4) a polypropylene connector body; 5) a quartz filter Teflon® support; 6) a quartz filter (0.3 µm pore diameter) to retain the insoluble fraction of total atmospheric deposition; 7) an O-ring to fix the quartz filter onto the support; 8) a filter polypropylene container; and 9) a 1 L receiving polyethylene bottle for the soluble fraction of atmospheric deposition.

A standard ICP–MS protocol for Cu(II), Mn(II), As(III), Cd(II), Pb (II), Sb(III), V(III), Sr(II), Co(II) and Rb(II) determination was applied on a PerkinElmer ELAN9000 equipment (Waltham, MA, USA). The instrument conditions and measurement parameters used in the analytical determination were 1000 W RF power, a carrier gas flow rate of 1 L min^{-1}, lens voltage of 7.25 V, a wash time of 35 s and three replicates for each sample. Quantification of elements was performed by an internal standard protocol with Y(III).

2.3. Experimental procedure for elemental fractionation in atmospheric deposition by the AEFS

A strict protocol for preparation and washing of the AEFSs was followed before field deployment for sampling. All parts were first washed in 2% aqueous solution of phosphate free Extran detergent (Merck, Darmstadt, Germany) for 24 h. Then the pieces were rinsed with water and placed in 9:1 HCl:ethanol bath for 24 h. Finally, the pieces were rinsed with suprapure water, dried under an extraction hood and stored in sealed bags until use.

47 mm diameter grade QMA quartz filters Whatman (0.3 µm pore diameter) (Maidstone, Kent, United Kingdom) were weighed and placed in AEFSs just before sampling. The AEFSs were then anchored to the top of a 2 m height pole and exposed to atmospheric deposition for one week. After the sampling period, the AEFSs were sealed in plastic bags and transferred to the lab.

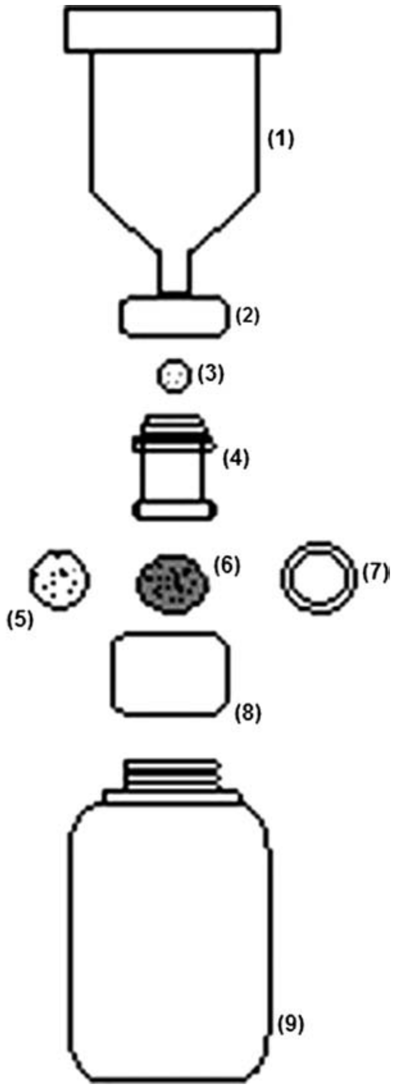

Fig. 2. AEFS scheme: 1) an upper bottle with funnel end (115 mm diameter, 300 mm height); 2) a connection ring; 3) a perforated disk aimed to retain extraneous matter (insects, leaves, straws and the like); 4) a connector body; 5) a 40 mm diameter quartz filter support (0.5 mm pore size); 6) a 47 mm diameter quartz fiber filter (0.3 μm pore diameter); 7) an o-ring; 8) a filter polypropylene container; and 9) a 1 L receiving bottle.

Table 1
Blank values and limits of detection (LODs) of the selected analytes in the soluble and insoluble fractions of the total atmospheric deposition samples. All results are in μg L^{-1}.

Elements	Soluble fraction blank	Soluble fraction LOD	Insoluble fraction blank	Insoluble fraction LOD
Mn	0.27	0.13	4.97	0.28
Cu	0.31	0.47	1.86	1.42
As	0.01	0.01	3.67	3.37
Cd	0.02	0.03	0.17	0.03
Pb	0.69	0.49	2.61	0.47
Sb	0.01	0.01	0.57	0.23
V	0.11	0.13	6.70	6.61
Sr	0.11	0.35	9.78	2.91
Co	0.07	0.02	0.16	0.09
Rb	0.03	0.03	2.29	1.47

200 mL of ultrapure water was carefully dispensed all around the upper polyethylene bottle to sweep along any particulates adsorbed onto the walls. Then the AEFS was dismounted to obtain the two atmospheric deposition elemental fractions as shown in Fig. 3; the insoluble fraction (IF) retained onto the quartz filter, and the soluble fraction (SF) collected in the receiving bottle.

The insoluble fraction collected on the quartz fiber filter was digested as described in [20]. Briefly, sampling filters were placed in Teflon® digestion vessels. 2.5 mL HNO_3 and 5 mL HF were added and the mix was left to react for some time. The vessels were then closed and heated up to 90 °C in a stove for 8 h. After cooling, the vessels were open, 2.5 mL $HClO_4$ was added and the solution was evaporated to dryness. 1 mL HNO_3 was added and the solution was again evaporated to dryness. The samples were finally taken with 2.5 mL HNO_3 and water to a total volume of 50 mL.

The soluble fraction collected in the receiving bottle was acidified with HNO_3 to pH 2 and assayed by ICP–MS. Average concentrations of each element in the soluble and insoluble blanks (Table 1) were subtracted from ICP–MS values obtained for the real samples in each corresponding fraction. Concentrations in μg m^{-2} week^{-1} were calculated considering the AEFS area (103.9 cm^2) and the weekly frequency of the sampling.

For the validation of the AEFS with the Coal Fly Ash 1633c certified reference material, 50 mg was dispersed inside the upper polyethylene bottle and the AEFS was processed as described for the field exposed AEFSs.

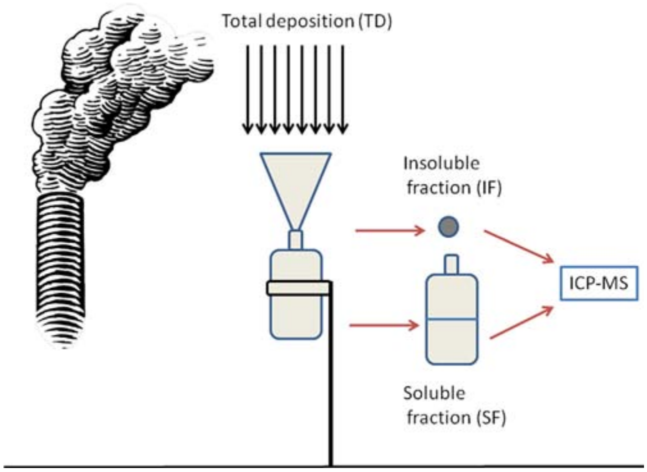

Fig. 3. Scheme of total atmospheric deposition sampling and elemental fractionation by the AEFS.

3. Results and discussion

3.1. Blank values and detection limits

The limits of detection (LODs) for the AEFS+ICP–MS methodology were estimated separately by applying the IUPAC definition to the selected analytes in the soluble fraction (SF) and in the insoluble fraction (IF) of the total atmospheric deposition. The LOD for the SF was estimated by assaying 10 solutions obtained after passing 200 mL suprapure water through 10 cleaned AEFS lined with blank quartz filters. The LOD for the IF was estimated by assaying 10 quartz fiber blank filters according to the described protocol. The estimated LODs are shown in Table 1. These values are appropriate for trace element measurements in SF and IF fractions of total atmospheric deposition samples collected in polluted and unpolluted locations.

Estimation of LODs was carried out using the EN-15841:2010 [14] standard for the determination of Pb, Cd, As and Ni in atmospheric deposition.

3.2. Validation of the AEFS with certified reference material samples

The AEFS was first tested in laboratory experiments by using the NIST Coal Fly Ash 1633c certified reference material, which is commercially available as a fine powder by testing the recoveries after assaying 10 independent samples. Each sample (50 mg) was carefully dispersed inside the upper polyethylene bottle, simulating atmospheric deposition, and processed as described in Section 2.3. Analytical results for the corresponding SF and IF fractions were measured for each trace element and converted to μg/g for comparison with the certified values. The results are summarized in Table 2.

The experimental results clearly demonstrated the usefulness of the proposed AEFS sampler for elemental fractionation of the simulated atmospheric deposition. Measurable SF and IF concentrations were obtained for all the elements assayed, with generally higher concentrations found in the IF fraction as expected from the certified reference material carbonaceous nature (the adsorbing capacity of carbonaceous materials is well documented). The sum of SF and IF fraction (TD column) for each of the elements assayed shows a good correlation with the certified values for elemental concentrations as depicted in Fig. 4, with excellent recoveries in most cases (slope 1.042). These results confirmed the potential applicability of the AEFS for the intended use of soluble and insoluble elemental fractionation in real atmospheric deposition.

3.3. Field testing of the AEFS for elemental fractionation in atmospheric deposition

After the successful lab testing with certified reference materials samples, a set of AEFSs were applied to elemental fractionation in real atmospheric deposition during a field campaign aimed to air quality measurement in the vicinity of the industrial complex Puchuncaví–Ventanas (V Region, Chile, see Fig. 1). A total of 14 atmospheric deposition samples were collected during the 2008 winter sampling campaign at the locations of La Greda (LG), Los Maitenes (LM), Puchuncaví (Pu) and Valle Alegre (VA), and processed according to the experimental protocol described in Section 2.3. The elemental deposition results obtained in the soluble (SF) and insoluble (IF) fractions, and the sum of both fractions (TD) are shown as averages and ranges in Table 3a (LG), b (LM), c (PU) and d (VA).

Table 2
Concentration of elements measured in the soluble (SF) and insoluble (IF) fractions and total (soluble + insoluble) concentration (TD) obtained during validation of the AEFS using Coal Fly Ash 1633c certified reference material. All results are in μg/g.

Elements	**Certified value**	**s**	**SF**	s	**IF**	s	**TD**	**s**
Mn	240.2	3.4	2.87	0.89	246.54	18.32	249.41	18.67
Cu	173.7	6.4	5.19	4.58	155.71	12.22	160.89	14.79
As	186.2	3	41.51	7.86	145.84	12.43	187.35	15.64
Cd	0.758	0.005	0.24	0.06	0.46	0.13	0.70	0.15
Pb	95.2	2.5	3.19	1.45	94.75	8.20	97.94	8.27
Sb	8.56	0.29	0.30	0.06	8.37	0.71	8.67	0.74
V	286.2	7.9	5.41	0.80	274.56	21.98	279.97	22.17
Sr	901	56	33.61	5.54	904.55	60.00	938.15	60.74
Co	42.9	3.5	0.39	0.46	38.36	2.97	38.75	2.93
Rb	117.42	0.53	0.80	0.17	121.12	8.45	121.92	8.44

s: standard deviation.

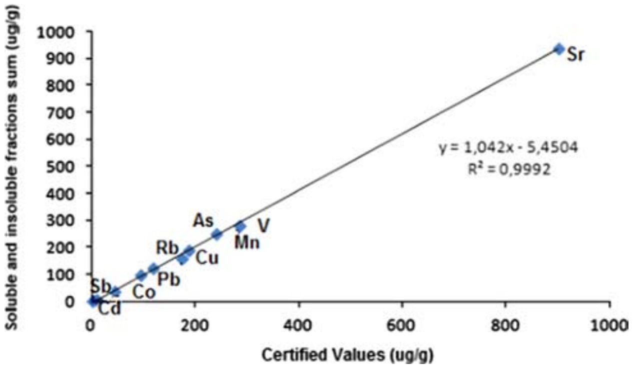

Fig. 4. Correlation between measured (SF + IF) and certified values for reference material Coal Fly Ash 1633c, during AEFS validation experiments.

The results obtained clearly demonstrate the potential of the AEFS for total atmospheric deposition measurement and elemental fractionation around the industrial complex. The highest total elemental atmospheric deposition (TD) was observed for all the selected analytes at La Greda, the most impacted location within the study area (1.8 km to the industrial complex, and under the influence of prevalent pollution dispersion by dominant SW winds). Lower TD values were measured at the intermediate pollution locations Los Maitenes (2.5 km to the industrial complex) and Puchuncaví (8.58 km to the industrial complex, but under the influence of prevalent pollution dispersion by dominant SW winds like La Greda location). The lowest TD values were measured at Valle Alegre location (6.43 km to the industrial complex, and isolated to the influence of pollution dispersion by dominant SW winds). Copper is the dominant element in the atmospheric deposition, especially in the LG and LM locations, closer to the industrial complex where a copper refinery is a major pollution source. The rest of the elements assayed follow a similar trend.

In general, a higher proportion of water-soluble metals is indicative of anthropogenic rather than crustal sources, since metals in anthropogenic particles consist of metal-dominated abrasion or hot-vapor condensation particles, or metals that have condensed onto the surface of other particles, and thus tend to be more labile than metal bound within crustal material [4]. The results provided by the AEFS show that Sr, As and Cd are the most bio-accessible elements in the atmospheric deposition at the study area, with water-soluble fractions in the range 50–65%. These results indicate the presence of soluble forms with a higher risk of transfer from atmospheric deposition to other environmental compartments. Scarce data of airborne Sr water solubility are available in the literature, but our results are comparable to those reported by Graney et al. [21] during a study on concentrations and solubility of metals from indoor and personal exposure PM2.5 samples. The results obtained for Cd and As are in agreement with previous studies on elemental fractionation that have reported high Cd solubility in water extracts from atmospheric particulate matter collected in the vicinity of anthropogenic sources [21–23]. Heal et al. [4] found around 50% water-soluble proportions for V, Zn, As and Cd in PM collected at urban locations. Our results show water extractable fractions in the range 30–50% for Mn, Pb, Sb, and Rb, indicating that these elements are present in rather inert, low soluble chemical forms, implying a moderate risk of transfer to the soil–groundwater–plant system. Similar results were found for Mn and Pb in the previously cited studies by Heal et al. [4] and Birmilli et al. [22]. Schneidemesser et al. [23], found a similar water extractability for Sb and Mn. From our results, Cu, V and Co are the lowest soluble elements with water-soluble fractions under 20%. Cu is very abundant element in the total deposition at the study area, due to the proximity of a copper refinery. Our results show a somewhat lower Cu water solubility than previously reported data for PM [4,22], but similar to the solubility value reported for urban PM2.5 by Fernandez-Espinosa et al. [6] and Schneidemesser et al. [23]. Literature data for V solubility are also contradictory, probably due to species variability depending on

Table 3
Mean deposition values and ranges for the elements analyzed in the soluble fraction (SF), insoluble fraction (IF) and in the total atmospheric deposition (TD) at sampling location La Greda (3A), Los Maitenes (3B), Puchuncaví (3C) and Valle Alegre (3D). All results are in μg m^{-2} $week^{-1}$.

Element	SF			IF			TD = SF + IF		
	Mean	Minimum	Maximum	Mean	Minimum	Maximum	Mean	Minimum	Maximum
3A									
Mn	173	151	194	379	194	513	552	366	664
Cu	4960	2710	7830	34,600	25,700	52,100	39,600	30,350	54,800
As	152	37.7	323	174	80.0	252	326	175	575
Cd	6.40	2.30	14.0	7.50	4.40	10.0	13.9	7.30	22.1
Pb	108	63.8	145	846	716	1060	954	861	1130
Sb	18.4	9.60	25.8	54.8	31.7	81.6	73.3	51.6	91.2
V	18.0	12.3	22.8	139	71.5	198	157	94.3	217
Sr	145	92.1	223	175	94.7	264	320	260	384
Co	5.6	2.70	10.6	26.7	18.9	40.6	32.3	24.1	43.3
Rb	12.3	440	24.7	369	22.0	40.8	49.3	30.0	65.6
3B									
Mn	75.5	56.7	102	132	89.2	189	207	146	257
Cu	3740	2210	6160	16,100	6730	25,200	19,800	9570	3130
As	137	96.9	186	122	44.9	181	259	230	278
Cd	2.80	0.20	5.40	3.50	1.30	6.70	6.30	1.50	12.1
Pb	126	51.6	216	388	261	613	514	342	828
Sb	21.9	11,4	27.6	39.5	11.7	67.8	61.3	39.3	94.4
V	11.6	7.00	16.7	51.3	44.1	57.0	62.8	59.6	68.0
Sr	107	38.4	196	45.8	4.60	83.5	153	42.9	246
Co	2.00	0,40	3.10	12.4	3.60	18.1	14.4	6.20	21.1
Rb	6.60	3.50	8.70	13.3	11.5	16.2	19.9	15.8	24.9
3C									
Mn	94.1	70.3	106	214	106	289	308	205	395
Cu	736	3550	1170	3320	2530	4190	4060	3340	4810
As	28.1	820	34.0	31.2	26.5	42.8	59.3	36.7	81.0
Cd	0.90	0.00	2.10	1.20	0.60	2.50	2.10	0.80	3.90
Pb	36.4	20.6	61.2	97.2	65.7	138	134	86.4	178
Sb	6.40	3.20	9.30	7.40	3.90	11.2	13.8	9.80	17.4
V	7.90	0.00	27.2	51.9	44.6	69.7	59.9	45.9	73.3
Sr	97.3	54.0	132	59.3	4.60	84.1	157	58.6	207
Co	0.20	0.00	0.60	10.3	8.00	13.1	10.4	8.00	13.1
Rb	3.90	1.80	6.60	18.4	14.8	20.7	22.3	19.6	24.1
3D									
Mn	69.6	28.6	124	90.2	30.4	182	160	59.0	226
Cu	782	324	1340	1610	473	2430	2400	997	3750
As	46.4	4.90	150.0	< LOD	< LOD	< LOD	55.8	14.3	1600
Cd	1.10	0.00	2.20	0.60	0.10	1.70	1.60	0.40	2.80
Pb	72.6	31.1	139	55.6	14.7	128	128	60.2	267
Sb	7.90	2.20	13.10	3.40	1.80	5.00	11.3	4.00	16.9
V	2.90	0.70	40.0	17.2	11.8	33.3	20.1	13.7	33.3
Sr	93.5	42.4	189	20.1	4.60	39.9	114	47.7	194
Co	1.30	0.40	40.0	5.40	3.60	10.8	6.70	3.60	10.8
Rb	7.10	2.40	9.40	6.60	1.60	11.5	13.7	6.90	20.9

particulate matter sources. We have measured a V water-soluble fraction amounting to 11–18%, in line with the values found by Schneidemesser et al. [23], but lower than the results obtained by Fernandez-Espinosa et al. [6]. The low solubility of Co found in our fractionation study (mean value 13.5%) is similar to the solubility reported by Schneidemesser et al. [23] in PM10 samples but lower than the result published for urban background PM by Birmilli et al. [22]. These results confirm the validity of the AEFS for in situ elemental fractionation of total atmospheric deposition samples.

4. Conclusions

An atmospheric elemental fractionation sampler (AEFS), consisting of a passive atmospheric total deposition collector modified with a quartz fiber filter (filtering-bulk), has been demonstrated for fractionation of elements contained in total atmospheric deposition, with potential applicability to "in situ" operation. The proposed fractionation sampler has been demonstrated as a significant advancement in pollution assessment in residential and remote areas, allowing the determination of soluble and insoluble forms of elements in atmospheric deposition. After sampling, soluble (SF) and insoluble (IF) fractions are separately assayed in the lab by appropriate pretreatment and by ICP–MS. Validation with certified reference material and proper operation during a field pollution assessment campaign demonstrate that the new sampler is a useful and affordable alternative to more sophisticated active sampler or automatic dry-only/wet-only collectors within short and long term atmospheric monitoring activities, especially for unattended and power free operation at remote places.

Acknowledgments

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