Rainwater analysis by synchrotron radiation-total reflection X-ray fluorescence

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ABSTRACT

Total reflection X-ray fluorescence analysis excited with synchrotron radiation was used to quantify the elemental concentration of rainwater in Córdoba, Argentina. Standard solutions with gallium as internal standard were prepared for the calibration curves. Rainwater samples of 5 μl were added to an acrylic reflector, allowed to dry, and analyzed for 200 s measuring time. The elemental concentrations of As, Ca, Co, Cr, Cu, Fe, K, Mn, Ni, Pb, S, Sr, V, and Zn were determined. The electrical conductivity, pH, and elemental concentrations were compared to data previously reported for the soluble fraction of rainwater at different sites. A factor analysis was performed in order to determine the sources that contributed to the elemental concentration in rainwater. Anthropogenic sources were identified as traffic pollution, vehicular emissions, and metallurgical factories. The quality of rainwater was analyzed by comparing the concentrations of all the elements in rainwater samples with the WHO guideline values for drinking water. The results show the need to control the atmospheric emissions in order to preserve the quality of rainwater. SR-TXRF analysis of chemical composition of rainwater in Córdoba represents the very first contribution in the region to the knowledge of the concentration of trace metals in the soluble fraction of rainwater. These data are scarce, especially in the Southern Hemisphere.

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Introduction

Anthropogenic activities affect the chemical composition of rainwater. Hence, the natural composition of rainwater is strongly related with the degree of air pollution. Anthropogenic sources have contributed to increase the trace metal concentration in the atmosphere. Therefore, concentrations of trace metals in rainwater can be good indicators of pollution coming from anthropogenic activities. In fact, recent studies are focused not only on determining the chemical composition of rainwater but also on explaining the sources responsible for the chemical elements in rainwater which is accomplished by applying different source apportionment techniques (e.g., [1]). This kind of studies is very scarce in south hemisphere (e.g., [2]).

Total reflection X-ray fluorescence (TXRF) is a suitable technique for identification and quantification of trace chemical elements due to its advantageous features, namely multielement capability, high sensitivity, precision, and short time of analysis ([3,4]). This is mainly because of the low background signal given by the poor penetration of X-rays into the substrate holder, the double excitation by the incident beam and the reflected beam from the substrate, and the optimization of the detection solid angle by the grazing incidence of the ionizing beam

(e.g., [5]). Different works show the applications of this technique in the analysis of rainwater. Stossel and Prange (1985) [6] use TXRF for the multielement determination of trace elements in rainwater in order to test three sample preparation techniques. Muia et al. (1991) [7] study different experimental conditions of TXRF for the determination of dissolved elements in rainwater in order to find the more suitable condition to perform the analysis. Hoffmann et al. (1997) [8] compare TXRF and ICP-MS in the analysis of rain and snow samples, finding that in the limits of twice the standard deviation most of the comparable results are identical. Holynska et al. (2004) [9] use TXRF to analyze the effect of acid rain on the deterioration of sandstone, material composing many buildings, and monuments. Montero Alvarez et al. (2007) [10] analyze rainwater by using TXRF and anodic stripping voltammetry, finding a good agreement between results obtained with both methods. TXRF combined with synchrotron radiation (SR) as excitation source offers new possibilities of reaching lower detection limits due to the high intensity, the linear polarization, and the natural collimation of the SR beam [5,11]. These advantages allow the use of SR-TXRF for analyzing trace chemical elements in rainwater, drinking water, sea water, and river water (e.g., [12,13]).

The aim of this work is to quantify the elemental composition of rainwater in the soluble fraction at Córdoba City (Argentina) using SR-TXRF and to identify the sources contributing to the chemical composition in rainwater. The knowledge of the chemical composition of rainwater and its sources is important in this area because surface water is used for human consumption, including drinking water.

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Experimental

Sampling data

The study was carried out in the City of Córdoba, which has an estimated population of 1.3 million; it is a mediterranean city located in a semiarid region in the center of Argentina (31.4°S; 64.18°W; 470 m.a.s.l.). The rainwater collection was carried out manually between October 2009 and July 2012 using a pre-cleaned polyethylene funnel of 53.5 cm in diameter connected to a pre-cleaned polyethylene bottle. The rain collection sampling was carried out from the start to the end of the rain event. Immediately upon collection, the electrical conductivity and pH were measured. The collected volumes were stored (refrigerated) at 4 °C until the samples treatment. The collected volume was filtered using Millipore membrane filters with a 0.45 μm pore size. After the filtration processes, rainwater samples were submitted to a slow evaporation process by boiling the water (e.g., [14]), reducing the original volume to 1/20–1/50. The evaporation process was carried out in a stepwise procedure in order to avoid the loss of sample during the evaporation. In order to avoid contamination, the devices involved in the evaporation process were carefully cleaned with Milli-Q water after the evaporation of each sample. In order to calculate the dilution factor, the final volume was measured for all the concentrated samples. A total of 69 rain events were sampled, which represents 66% of the total rainy days of the sampling period. This percentage was considered representative of the rainy days since (a) rainy days were discarded when the precipitation depth was lower than 1 mm and (b) two consecutive rainy days were considered as a unique rainy event.

Instrumentation

pH and electrical conductivity

The pH and electrical conductivity measurements were performed by using a calibrated Accumet AR20 (Fisher Scientific, USA) instrument. Buffer solutions of pH 4.00, 7.00, and 10.00 were used to calibrate the instrument prior to each measurement.

SR-TXRF analysis

Samples were analyzed by SR-TXRF using the XRF beamline at the Brazilian Synchrotron Light Source Laboratory (LNLS), in Campinas (Brazil). All measurements were performed under normal environmental conditions of pressure and temperature. The samples were excited with a polychromatic beam (energy from 2 to 24 keV), in grazing incidence, 2 mm in height and 5 mm in width. A Si(Li) detector with a nominal energy resolution of 165 eV at 5.9 keV (Mn Kα line) was used, and the integration time was 200 s. The detector was located at 5 mm over the sample, approximately at 90° with respect to the direction of incidence. In order to keep the dead-time below 20% a 1 mm collimator was used in front of the detector.

Sample and standard preparation

A multielemental standard solution (Merck 109498) containing 29 elements at 10 mg l^{-1} was used as standard solutions (reference solutions). The analyzed elements were As, Ca, Co, Cr, Cu, Fe, K, Mn, Ni, Pb, S, Sr, V, and Zn. This solution was diluted between 10000 and 0.2 μg l^{-1} to perform the calibration curves. Considering that the multielemental solution does not contain sulfur, a standard solution was prepared by dissolution of anhydrous Na_2SO_4 (Merck 106649) in Milli-Q water. A volume of Ga-standard solution was added as internal standard to have 10 μg l^{-1} Ga concentration in every sample. After Ga was added to each standard solution and rainwater sample, 5 μl of this solution was deposited on an acrylic reflector of dimensions [2 × 3 × 0.2] cm³ and was allowed to dry. The same procedure was followed for a reference blank, which was prepared with Milli-Q water.

The detection limit for each element (DL_i) was calculated following Eq. (1):

$$DL_i = 3\sqrt{\frac{I_{BG}}{t}}\frac{C_{Ga}S_{Ga}}{I_{Ga}S_i} \tag{1}$$

where I_{BG} is the background intensity, t is the measuring time, in seconds, C_{Ga} is the Ga concentration, I_{Ga} is its fluorescent intensity, S_{Ga} is its sensitivity, and S_i is the sensitivity of an element i [11,15].

Spectra analysis

Spectra were analyzed with the AXIL package [16]. The blank spectrum structure was subtracted in all analyzed spectra. As an example, Fig. 1 shows the normalized TXRF spectra of a rainwater sample. Some of the peaks corresponding to different elements have been highlighted. The relative intensity of the Kα (Lα) line of the studied elements (Pb) was calculated, i.e., the ratio between the fluorescent intensity of the element i and Ga. Fig. 2 shows the correlation between the relative intensities and the multielemental standard concentration for V, Mn, Co, Ni, Cu, and Zn. For each element, a calibration curve was constructed using a linear fitting; the square-correlation factor (R^2) was higher than 0.90 for all the calibration curves. All the studied elements except Ca were quantified using the calibration curves. Ca cannot be quantified following the procedure previously detailed because even though Ca is present in the multielemental standard solution, it is present in low concentrations. For this reason, Ca was quantified using the elemental sensitivity method [16]. As an example, Fig. 3 shows the relative intensities versus the atomic number (Z), for a standard solution of 10 mg l^{-1} in concentration. These data of all the standard concentrations were fitted using a second order exponential function in order to interpolate the intensities of Ca (Z = 20) and the corresponding calibration curve were then obtained. The errors associated to each concentration value were calculated by considering both the experimental and fitting errors. The experimental errors include those involved with the sample collection, filtration, and concentration processes, volume measurements, and standard solution preparation, while the fitting errors are those involved in the fitting of the spectra by using the AXIL software and the fittings involved in the elemental sensitivity method and the calibration curves.
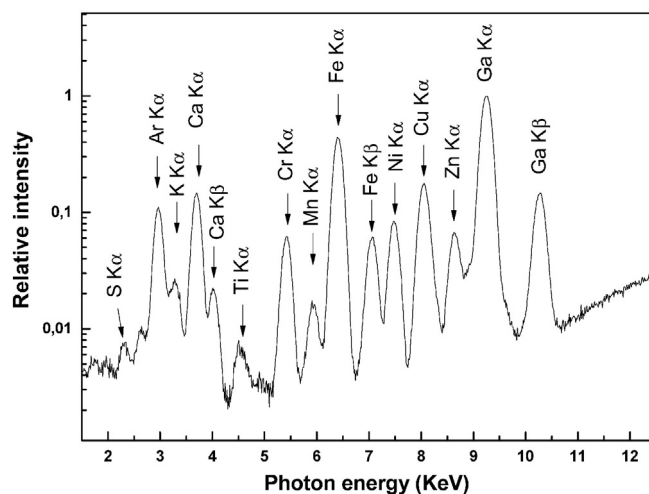

Fig. 1. Normalized SR-TXRF spectrum of a rainwater sample. Fluorescent emission lines of elements found in this sample are indicated: S, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, and Zn. Ga is the internal standard, and Ar is present since measurements were performed under normal environmental condition of pressure.
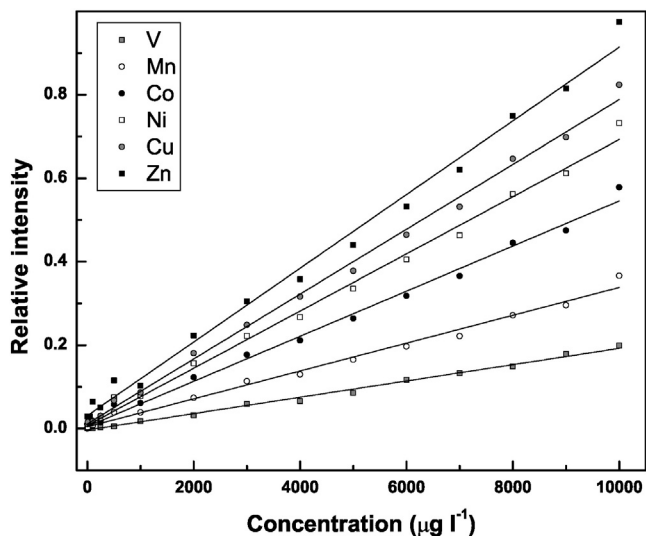
Fig. 2. Evolution of the relative intensities versus the standard solution concentrations for V, Mn, Co, Ni, Cu, and Zn.

Results and discussions

Rainwater chemical composition

The volume-weighted mean (VWM) for the elemental concentrations, pH, and electrical conductivity (EC) values was calculated as

$$VWM = \frac{\sum_{i=1}^{N} w_i x_i}{\sum_{i=1}^{N} w_i} \qquad (2)$$

where x_i is the elemental concentration, pH, or EC value of the ith sample, w_i is the precipitation depth of the ith sample, and N is the total number of samples. In order to analyze the magnitude of pH, EC, and the elemental concentration, VWM values obtained in this work were compared to data previously reported for soluble fraction of rainwater at different sites. Table 1 shows the detection limits for each element analyzed, the values of elemental concentrations, pH, and EC measured in
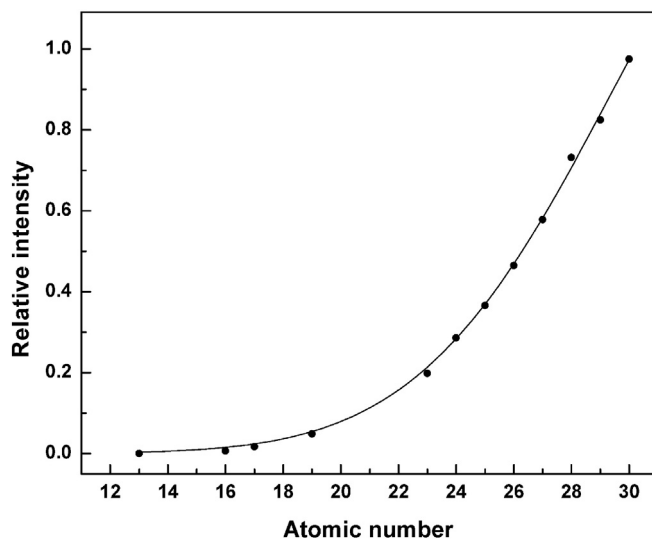

Fig. 3. Relative intensities versus the atomic number for elements in the standard solution at 10 mg l^{-1}. Experimental data were fitted using a second order exponential function.

this work, the propagated VWM experimental error, and the elemental concentration, pH, and EC reported in other studies with different characteristics: Tabatinga [17], in Amazonas, as a background site; a rural site in Mexico [18]; Mersin, in Turkey, as an urban site [19]; and Mexico, as a highly polluted city [20]. In the present work, the quantification method measures the S-elemental concentration, that is, the total sulfur contained in all the S-species. To make the comparison possible, it is assumed that the predominant species containing S is SO_4^{2-}.

The results from Table 1 show that trace metal concentration values for Córdoba are in the range of values reported for Tabatinga (background site) and Mersin (urban site). Differences regarding Ca and K concentrations can be explained considering the variability in the characteristics of the studied sites (mediterranean, coastal, and desert sites).

The composition of trace metals in rainwater over Córdoba is lower than those reported for Mexico City, which is one of the largest megacities in the world with a very polluted atmosphere.

Table 1 shows that the average pH obtained in Córdoba is a little larger than that reported in the other studies. In fact, the pH varied from 4.76 to 7.50, reflecting mainly an alkaline regime. This result is expectable, considering that Córdoba presents low levels of tropospheric pollutants like $SO_{2(g)}$ and $NO_{2(g)}$ [21,22]. The alkaline regime can be explained considering that precipitation could effectively scavenge the Ca-bearing compounds existing as coarse particles in the atmosphere [23].

The electrical conductivity value in Córdoba is slightly higher compared to that of Tabatinga. Tabatinga has a low ion concentration and has one of the most pristine rainwater environment in western Amazonia [17]. Considering this fact, ion concentration in rainwater at Córdoba is not greatly impacted by the urban environment of the city.

Rainwater quality

There are not any international guidelines for rainwater quality. However, the quality of rainwater was analyzed by comparing the VWM values obtained in this work with the guidelines values for drinking water quality established by the World Health Organization [24]. This comparison is particularly important in Córdoba, considering that surface water is used as a source for numerous domestic applications like recreational activities, laundry, gardening purposes, and drinking water. The concentrations of Cr, Ni, Cu, and Pb in rainwater samples are consistently lower than the WHO guideline values for drinking water, which are 10, 50, 70, and 2000 µg l^{-1}, for Pb, Cr, Ni, and Cu, respectively. WHO does not establish guideline values for naturally occurring chemicals and for elements which are not hazardous to health. Thus, it can be concluded that for the analyzed elements and even though it is affected by the air pollution, rainwater is acceptable for human consumption. However, control on the atmospheric emissions is needed in order to preserve the quality of rainwater in Córdoba.

Temporal variability

The inter-annual chemical composition of precipitation was analyzed. Because rains are scarce or even absent during the dry season, data are too few to obtain meaningful statistics regarding seasonal effects. Statistical parameters of the elemental concentrations, pH, and EC values for the hydrological years (September 1st to August 31th) in the sampling period are shown in Table 2. ANOVA statistical analysis showed that there are no significant differences between the three hydrological years (significance level = 0.05), except for S, and pH which were different for the period 2010–2011. Assuming that the predominant specie containing S is SO_4^{2-}, the decrease in pH can be explained considering the increase in SO_4^{2-} concentration. Two sources were proposed to explain this increase: (1) biomass burning, because the highest S concentration was found on June 2010, immediately after a biomass burning registered in the hills surrounding Córdoba City and reported in the local graphical media, and (2) volcanic emissions, because

Table 1
Detection limits, volume-weighted mean concentrations (VWM), and experimental errors for each element measured at Córdoba City. Comparison with VWM concentrations reported from different locations around the world.

Element/specie	Units	VWM concentration		Tabatinga, Amazonia [17]	México, rural site [18]	Mersin, Turkey [19]	México, urban site [20]
		This study					
		DL					
SO_4^{2-}	$\mu Eq\ l^{-1}$	0.43	40 ± 2	3.8	56.1		61.94
K^+	$\mu Eq\ l^{-1}$	0.09	13 ± 3	2	5.27	4.61	2.16
Ca^{2+}	$\mu Eq\ l^{-1}$	0.08	120 ± 20	9.2	7.67	194.5	26.44
As	$\mu g\ l^{-1}$	0.18	<DL				
V	$\mu g\ l^{-1}$	0.50	0.77 ± 0.07	0.05	3.43		4.78
Cr	$\mu g\ l^{-1}$	0.35	0.60 ± 0.09		0.28	1.05	0.26
Mn	$\mu g\ l^{-1}$	0.30	0.7 ± 0.2	0.66	6.05	3.23	8.34
Fe	$\mu g\ l^{-1}$	0.24	10.2 ± 0.1	19.99		3.21	
Co	$\mu g\ l^{-1}$	0.20	<DL			1.35	
Ni	$\mu g\ l^{-1}$	0.17	0.36 ± 0.09	0.59	1.41	2.58	2.98
Cu	$\mu g\ l^{-1}$	0.16	3.9 ± 0.6	1.27		1.62	
Zn	$\mu g\ l^{-1}$	0.16	1.8 ± 0.2	7.65		36.9	
Sr	$\mu g\ l^{-1}$	0.50	3.7 ± 0.3	1.31		12.6	
Pb	$\mu g\ l^{-1}$	0.85	2.7 ± 0.8	0.21	0.76	5.07	1.58
pH			6.49	6.1	4.54	6.2	5.08
EC	$\mu S\ cm^{-1}$		8.70	5.8	23.81		

volcanic emissions are a source of SO_2. We conjecture that biomass burning is a probable source since it is an important source of SO_2 ([25] and references therein, [26]). Ashes from the eruption at the complex of Puyehue-Cordón Caulle volcano (e.g., [27]), sited around 1250 kilometers from Córdoba City, reached Córdoba's atmosphere on June 2011. Therefore, the rise in S concentration can be also related to this source. Except for these probable and punctual sources, the temporal analysis shows that the emissions affecting rainwater composition in Córdoba have a similar behavior among the years of study.

Source contribution

In order to study the possible sources of the reported elements, a factor analysis was performed online by using the Wessa Free Statistics Software [28]. For a factor, a physical interpretation of sources is possible by comparing the elements having high correlation in a particular factor with elements associated with known possible sources. For the factor analysis, Cr, Co, and As were not considered because they present null or very low variability. Thus, electrical conductivity, S, K, Ca, V, Mn, Fe, Ni, Cu, Zn, Sr, and Pb concentrations were the discriminating variables. Those concentration values below the detection limit were

Table 2
Comparison of arithmetic mean concentrations and their standard deviation (SD) of elemental concentration, pH, and electrical conductivity for the three hydrological years.

Element	Units	2009-2010		2010-2011		2011-2012	
		Media	SD	Media	SD	Media	SD
S	$\mu g\ l^{-1}$	965	1578	1063	1047	722	483
K	$\mu g\ l^{-1}$	806	911	625	594	648	726
Ca	$\mu g\ l^{-1}$	3854	2727	3508	2423	2879	2031
As	$\mu g\ l^{-1}$	<DL		<DL		<DL	
V	$\mu g\ l^{-1}$	1.72	4.23	1.16	1.76	0.94	1.36
Cr	$\mu g\ l^{-1}$	0.30	0.99	<DL		2.02	7.90
Mn	$\mu g\ l^{-1}$	0.64	2.37	2.28	8.59	1.00	3.98
Fe	$\mu g\ l^{-1}$	8.40	19.6	6.03	25.3	21.8	75.7
Co	$\mu g\ l^{-1}$	<DL		<DL		<DL	
Ni	$\mu g\ l^{-1}$	0.34	1.26	0.49	2.44	0.24	1.07
Cu	$\mu g\ l^{-1}$	2.50	4.76	3.90	14.5	5.17	16.6
Zn	$\mu g\ l^{-1}$	2.79	7.98	4.36	14.4	4.27	15.5
Sr	$\mu g\ l^{-1}$	3.23	6.15	4.48	8.26	2.24	3.94
Pb	$\mu g\ l^{-1}$	7.72	8.64	5.31	9.59	3.33	7.70
pH		6.64	0.44	6.05	0.69	6.45	0.51
EC	$\mu S\ cm^{-1}$	10.79	15.04	11.64	8.49	10.73	6.09

considered as one-half of the respective detection limit for statistical calculation (e.g., [19]). Varimax rotation was performed to maximize the variances of the squared factor loadings across variables for each factor. This method was applied to make the pattern of loadings clearer. It was found that four factor groups account for 65% of variance, i.e., four factors explain 65% of the sources contributing to the chemical composition in rainwater. Table 3 shows the factor loadings normalized with the Varimax rotation, the percentage of variance explained by each factor, and the probable sources related to the factors. When certain element is related to a factor (source), it presents a high (greater than 0.5) or moderate (between 0.4 and 0.5) loadings regarding that factor. As an example, in Factor 1, the electrical conductivity, S, K, Ca, and Sr are highly loaded (i.e., highly correlated). Observe that S and Ca are highly loaded in Factors 1 and 2. This behavior suggests dual sources for S and Ca.

Factors were associated to sources based on the elements related to each factor, the knowledge of the site, and the literature referring to elements considered as tracers of different sources. Factor 1 was associated to the leaching of atmospheric dust since it is mainly constituted by particles originated from natural sources. In fact, the correlation between Ca and SO_4^{2-} ($R^2 = 0.54$) suggests an important contribution from gypsum dissolution (e.g., [29]). Ca and Sr show a good correlation ($R^2 = 0.52$), which are mainly crustal originated elements. Factor 2 was associated to traffic pollution because Ni, V, and S are present in motor vehicle exhaust or produced through brake wear, tire wear, road dust resuspension, and other motor vehicle actions (e.g., [30]). Pb is mostly emitted from combustion of fuel and lubricant oil and from brake wear and wheel weights (e.g., [31]). V as vanadium oxide is a component of different kinds of steel used in automobile parts [18]. The loading of Ca indicates that this source could be mixed with cement factories [25]. Fe and Mn link Factor 3 to vehicular emissions (e.g., [25,32]) because the gasoline vehicle is characterized by high emissions of Mn and Fe. Furthermore, Mn is a known knock improver usually used in the gasoline car at trace concentration levels in order to improve the octane number of the fuel (e.g., [33]). The high loadings of Cu and Zn indicate that the source related to Factor 4 can be metallurgical factories (e.g., [25], and references therein).

Factors 2, 3, and 4 indicate that anthropogenic sources are probably responsible for the levels of some trace metals measured in rain samples. The results presented in this work were compared to those presented by López et al. (2011) [34] and Achad et al. (2014) [35], who reported the elemental composition of particulate matter in different size fractions. By this comparison, the presence of heavy metals is expected considering that they have been reported in aerosols, for PM10, PM2.5, and smaller size fractions.

Table 3
Varimax factor loadings, the percentage of variance explained by each factor, and the probable sources related to the factors. When elements present high loadings (i.e., high correlations) regarding a factor, the loadings are stressed in bold.

	Factor 1	Factor 2	Factor 3	Factor 4
EC	**0.865**	0.131	0.066	0.051
S	**0.511**	**0.781**	0.015	−0.09
K	**0.846**	0.196	0.065	−0.089
Ca	**0.546**	**0.580**	0.195	−0.054
V	0.050	**0.741**	0.303	0.233
Mn	−0.001	0.244	**0.701**	−0.144
Fe	0.033	0.010	**0.787**	−0.058
Ni	−0.136	**0.656**	−0.347	−0.239
Cu	−0.092	0.019	−0.124	**0.593**
Zn	−0.006	0.009	−0.005	**0.769**
Sr	**0.829**	−0.038	−0.069	−0.090
Pb	0.147	**0.635**	0.339	0.116
Variance (%)	23	20	13	9
Source	Atmospheric dust	Traffic pollution	Vehicular emissions	Metallurgical factories

Summary and conclusions

Elemental concentration values were obtained and compared to data previously reported for the soluble fraction of rainwater at different sites. The comparison shows that the elemental concentrations obtained in the present work are similar to the concentration values measured in other locations. The average pH was 6.34, which is slightly higher compared to other cities, reflecting mainly an alkaline regime. The concentrations of Cr, Ni, Cu, and Pb in rainwater samples are consistently lower the WHO guideline values for drinking water. In this way, results of the present study contribute to show to local and national authorities the need to set regulations for emissions and to control the atmospheric emissions in order to preserve the purity of rainwater. The temporal analysis shows that the elemental concentrations were similar for all the hydrological years, excepting S and pH. Therefore, it can be concluded that the atmospheric emissions responsible for the chemical composition in rainwater are constant for the analyzed years. A multiple correlation analysis was used to assess the sources of pollutants in precipitation. Factor analysis associates K and Sr to atmospheric dust, while S and Ca are related to both anthropogenic and crustal sources. On the other hand, Mn, Fe, Pb, Zn, Cu, Ni, and V were only related to anthropogenic sources. Anthropogenic sources were identified as traffic pollution, vehicular emissions, and metallurgical factories. They are in agreement to sources previously related to the particulate matter in Córdoba City.

SR-TXRF analysis allowed to gain an initial understanding of the rainwater chemistry in Córdoba and to quantify the elemental concentration of trace metals. This fact is particularly important since this is one of the few studies analyzing the composition of trace metals in the soluble fraction of rainwater. These data are scarce, especially in the Southern Hemisphere.

Acknowledgments

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