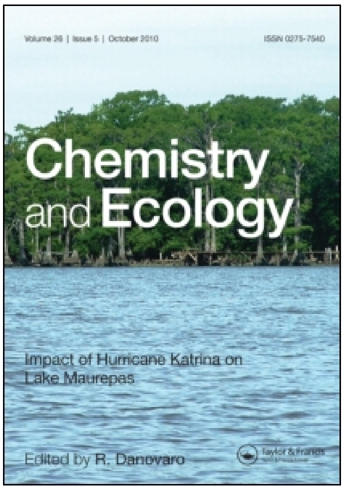

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Trace metals and inorganic ion measurements in rain from Mexico City and a nearby rural area

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Trace metals and inorganic ion measurements in rain from Mexico City and a nearby rural area

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Rain is a main source of water for the ecosystem in Mexico. Emitted particulate matter and gases enter the ecosystem by rain scavenging. Although the chemistry of rainwater has been the subject of a number of studies, the insoluble fraction has been virtually ignored. This fraction is made up of particulate material, and can be significant, particularly in rural forest regions. Average aluminium weights were the highest of all elements, in both the soluble and insoluble fractions. Ions with the highest concentrations were SO_4^{-2} and NO_3^-, followed by NH_4^+, Na^+, Cl^-, Ca^{2+}, Mg^{2+} and K^+. The Spearman rho correlation showed that the acidity was caused by SO_4^{-2} and NO_3^-, and the most important neutralising ion was NH_4^+. High crustal enrichment factors (EF_{crust}s) suggested that Mexico City in general was richer in Cd, Cr, Mn, Pb, and V than Rancho Viejo. The enrichment factors support the idea that the metals observed in rainwater have an anthropogenic origin. Air mass back trajectories were associated with the concentrations of trace metals and of SO_4^{2-}, Ca^{2+}, Mg^{2+}, and NH_4^+ observed during each rainy day.

Keywords: trace metals; inorganic ion measurement; wet precipitation; anthropogenic sources; enrichment factors.

1. Introduction

The study of trace metals in wet and dry precipitation has increased during recent decades because trace metals have adverse environmental and human health effects. Some metals, such as Pb, Cd and Hg, among others, accumulate in the biosphere and can be toxic to living systems. Anthropogenic activities have substantially increased trace metal concentrations in the atmosphere. In addition, acid precipitation promotes the dissolution of many trace metals, which enhances their bioavailability.

In recent decades, heavy metal concentrations have increased not only in the atmosphere but also in pluvial precipitation. Metals such Pb, Cd, As, and Hg are known to accumulate in the biosphere and to be dangerous for living organisms, even at very low levels [1].

Many human activities play a major role in global and regional trace element budgets [2–6]. Also, when present above certain concentration levels, trace metals are potentially toxic to

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marine and terrestrial life. Biogeochemical perturbations are a matter of crucial interest in science [7].

The atmospheric input of metals exhibits strong temporal and spatial variability due to short atmospheric residence times and meteorological factors [8]. As in oceanic chemistry, the impact of trace metals in atmospheric deposition cannot be determined by a simple consideration of global mass balance; rather, accurate data on net air or sea fluxes for specific regions are needed [9].

Particles in urban areas represent one of the most significant atmospheric pollution problems, and are responsible for decreased visibility and other effects on public health, particularly when their aerodynamic diameters are smaller than 10 μm, because these small particles can penetrate deep into the human respiratory tract [10,11].

Natural sources of aerosols include terrestrial dust, marine aerosols, volcanic emissions and forest fires. Anthropogenic particles, on the other hand, are created by industrial processes, fossil fuel combustion, automobile mufflers, worn engine parts, and corrosion of metallic parts [12,13]. The presence of metals in atmospheric particles increases their potential toxicity and the associated health risks [14,15].

The objective of this work is to investigate for the first time the chemical composition of the soluble and insoluble fraction of the rainwater collected in an urban area, Mexico City (at the Centro de Ciencias de la Atmósfera of the Universidad Nacional Autónoma de México), and a rural forest region, Rancho Viejo, in the Mexico State. Our study is basesd on the hypotheses that the dry deposition (i) contributes to the high concentration the trace metal in the insoluble fraction of the rainwater, and (ii) not only affects the air quality at local scale but can also influence the adjacent areas due to the wind's effects.

2. Methods and materials

2.1. *Sampling*

Sampling took place at two sites, one urban and one rural. The Rancho Viejo (RV) sampling site was located in a rural forested region situated at 19.10° N, 99.91° W, about 80 km southwest of Mexico City, in the State of Mexico, with no pollution sources, but downwind of Mexico City. The site is 2700 m above sea level with a mean rainfall of 1400 mm. During the rainy season, predominantly easterly winds at 700–600 mb transport air pollutants emitted from Mexico City and the city of Toluca to the site (Figure 1). Fifty-one wet precipitation samples were collected at the RV site per event.

The Mexico City (MC) sampling site was on the roof of the Centro de Ciencias de la Atmósfera (Atmospheric Science Center) building at the Universidad Nacional Autónoma de México campus, located at 19°19.57' N, 99°10.55' W in the south of Mexico City, 2200 m above sea level (masl). Mean rainfall is 800 mm. The site has green areas with moderate traffic surround the building (Figure 1). At the MC site, 107 samples were collected daily from mid-May to the end of October in 2003 and 2004.

Sampling was done with two automatic wet/dry precipitation collectors (Andersen, General Metal Works, Inc.). One collector was used to collect samples for trace metal analysis in soluble and insoluble fractions. The other was used to collect samples for ion analysis (SO_4^{-2}, Cl^-, NO_3^-, Ca^{2+}, Mg^{2+}, Na^+, K^+ and NH_4^+) in soluble fractions. To avoid artifacts, the lid arms on both collectors were coated with Teflon and the buckets were tightly sealed with polyethylene covers. All samples were sent to the analytical chemistry laboratory at the Centro de Ciencias de la Atmósfera. Precipitation samples were filtered through a 0.4 μm polycarbonate membrane filter. Samples were preserved at 4 °C until analysis.

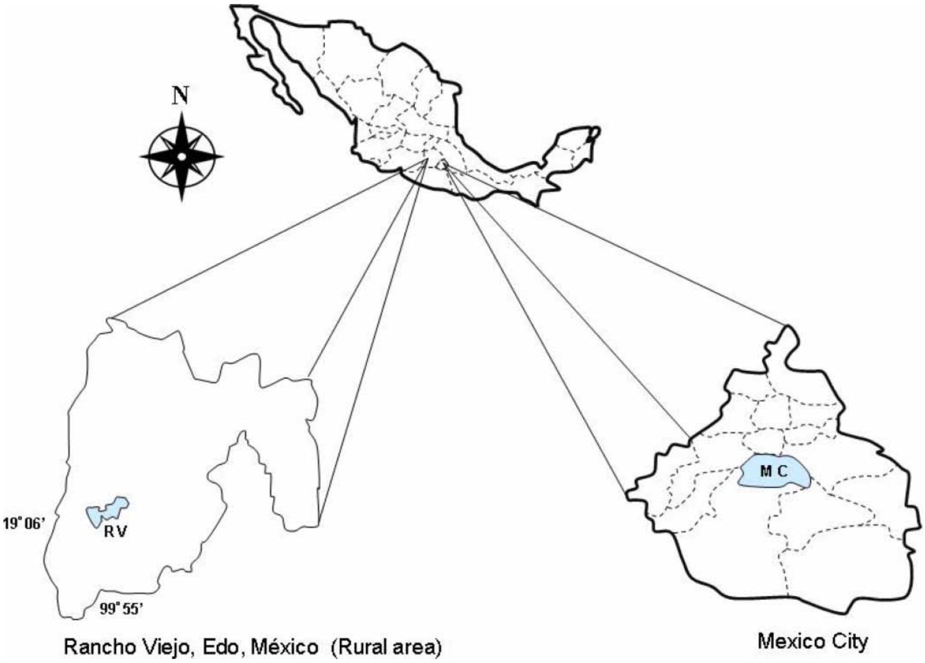

Figure 1. Sampling site locations (RV and MC).

Filters with the insoluble fraction were digested in a microwave oven, and the filtered solutions were poured into 25 ml volumetric flasks with deionised water to the mark. Solutions were used to determine the insoluble metal fractions. Heavy metal analysis was done using an atomic absorption spectrophotometer.

2.2. *Quality control*

Blanks on glass and plasticware were prepared and analysed. Blank concentrations for major ions and trace metals were below equipment detection limits.

Measurement precision and bias were determined using quality control check samples prepared in the laboratory. Ten replicate measurements were made for each ion and metal. Precisions, based on standard deviations of the measurements, were 0.48, 0.072, 0.04, 0.005, 0.014, 0.067, 0.006, and 0.032 mg l^{-1} for SO_4^{2-}, Cl^-, NO_3^-, Na^+, K^+, Ca^{2+}, Mg^{2+} and NH_4^+, respectively. Biases, in the same order, were 0.2, 0.52, −0.71, 6.3, −3.1, 2, 2.7 and 8.9%. Precisions were 1.54, 0.025, 0.22, 1.63, 0.27, 0.17, 0.27, and 0.97 μg l^{-1} for Al, Cd, Cr, Fe, Mn, Ni, Pb and V, respectively. Biases, in the same order, were 2.6, −0.31, 2.49, 2.8, −5.2, −3.76, 0.21 and −1.6%.

2.3. *Analytical procedures*

Chloride, NO_3^-, and SO_4^{2-} were analysed by non-suppressed ion chromatography with a Perkin Elmer liquid chromatograph equipped with a LC isocratic pump, an LDC analytical monitor III conductivity detector, and a Hamilton PRPX-100 analytical strong-anion column. Injection volume was 100 μl, and flow rate was 2 ml min^{-1} (Metrohm method). Ammonium was analysed by suppressed chromatography. The analytical setup was: Hamilton PRPX-200 analytical column, Alltech 335PCS suppressor module, Alltech cation suppressor cartridge, and a flow rate of 2 ml min^{-1} (Hamilton method).

Sodium, K^+, Ca^{2+} and Mg^{2+} were analysed with a GBC 932A double beam atomic absorption spectrophotometer. Deuterium and hollow cathode lamps (Photron Super lamp) were used for background correction and analysis.

Calibration standards were prepared from certified standards for each ion (High-Purity Standards traceable from the National Institute of Standards and Technology, NIST). The detection limits in mg l^{-1} were: 0.22, 0.04, 0.31, 0.002, 0.006, 0.01, 0.002, and 0.05 for SO_4^{2-}, Cl^-, NO_3^-, Na^+, K^+, Ca^{2+}, Mg^{2+} and NH_4^+, respectively.

Heavy metal analysis was carried out using an atomic absorption spectrophotometer (model GBC) with a 932AA double beam, coupled with a System 3000 graphite furnace accessory. Calibration standards were prepared with the same acid concentration as the samples, using certified standards for each metal (High-Purity Standards traceable from the National Institute of Standards and Technology, NIST). Standard addition methods were used for a cross check. The detection limits, in µg l^{-1}, were Al = 6.03, Cd = 0.07, Cr = 0.38, Fe = 2.04, Mn = 0.46, Ni = 0.78, Pb = 1.14 and V = 3.12.

3. Results and discussion

3.1. *Statistics*

Tables 1a, 1b, 2a, and 2b show the averages, standard deviations, minimums and maximums of ion and trace metal concentrations in insoluble and soluble fractions for the RV and MC sites, respectively, from 2003 to 2004.

Table 1a. Average, standard deviation, minimum and maximum concentrations (mg l^{-1}) of inorganic ions in rainwater (soluble fraction) at Rancho Viejo, 2003–2004 ($N = 51$).

Ion	Average	SD	Minimum	Maximum
SO_4^{2-}	1.73	0.25	0.22	0.08
Cl^-	0.27	0.08	0.07	2.64
NO_3^-	1.34	0.17	0.31	5.59
NH_4^+	0.64	0.09	0.05	2.81
Na^+	0.09	0.03	0.01	0.90
K^+	0.25	0.09	0.02	4.88
Ca^{2*}	0.16	0.03	0.006	3.15
Mg^{2+}	0.074	0.02	0.003	0.31
pH	4.92	0.37	4.10	5.91

Table 1b. Average, standard deviation, minimum and maximum concentrations (mg l^{-1}) of inorganic ions in rainwater (soluble fraction) at Mexico City, 2003–2004 ($N = 107$).

Ion	Average	SD	Minimum	Maximum
SO_4^{2-}	2.37	0.22	0.34	8.82
Cl^-	0.38	0.05	0.08	2.45
NO_3^-	2.64	0.25	0.47	5.58
NH_4^+	1.46	0.12	0.054	2.52
Na^+	0.31	0.09	0.008	2.92
K^+	0.09	0.008	0.006	0.46
Ca^{2*}	0.20	0.03	0.03	2.68
Mg^{2+}	0.04	0.005	0.005	0.22
pH	5.75	0.62	4.10	6.89

Table 2a. Average, standard deviation, minimum and maximum concentrations ($\mu g\, l^{-1}$) of the trace metal determined (insoluble, soluble and total rain fractions) in rainwater at Rancho Viejo, 2003–2004 ($N = 51$).

Metal	Fraction	Average	SD	Minimum	Maximum
Al	Insoluble	81.51	10.24	11.26	178.82
	Soluble	25.70	3.81	5.63	55.08
	Total	107.22	13.60	28.80	222.68
Cd	Insoluble	1.28	0.32	0.10	3.04
	Soluble	0.18	0.06	0.03	0.95
	Total	1.48	0.38	0.17	3.65
Cr	Insoluble	0.99	0.14	0.40	3.44
	Soluble	0.50	0.10	0.19	0.78
	Total	1.50	0.23	0.66	3.71
Fe	Insoluble	62.84	8.12	15.15	376.91
	Soluble	24.13	3.30	5.60	71.98
	Total	86.97	10.77	24.21	448.89
Mn	Insoluble	6.93	1.20	1.46	13.42
	Soluble	0.64	0.48	0.05	5.25
	Total	7.60	1.20	1.99	15.43
Ni	Insoluble	1.70	0.28	0.18	4.94
	Soluble	1.30	0.31	0.40	2.82
	Total	3.00	0.60	1.19	7.0
Pb	Insoluble	2.09	0.28	0.64	4.64
	Soluble	0.33	0.02	0.05	2.57
	Total	2.43	0.29	0.70	5.41
V	Insoluble	6.30	1.20	1.71	11.29
	Soluble	0.22	0.01	0.03	2.70
	Total	6.52	1.21	2.06	11.70

Table 2b. Average, standard deviation, minimum and maximum concentrations ($\mu g\, l^{-1}$) of the trace metal determined (insoluble, soluble and total rain fractions) in rainwater at Mexico City, 2003–2004 ($N = 107$).

Metal	Fraction	Average	SD	Minimum	Maximum
Al	Insoluble	61.03	5.53	9.03	89.95
	Soluble	22.91	2.40	7.07	51.74
	Total	83.94	7.55	35.83	125.37
Cd	Insoluble	0.74	0.11	0.055	9.85
	Soluble	0.12	0.02	0.035	0.92
	Total	0.88	0.13	0.115	9.94
Cr	Insoluble	0.86	0.10	0.20	3.24
	Soluble	0.37	0.039	0.038	1.68
	Total	1.24	0.133	0.33	4.59
Fe	Insoluble	54.60	4.86	23.55	79.55
	Soluble	22.75	1.91	8.63	39.62
	Total	77.34	6.58	35.32	117.42
Mn	Insoluble	11.72	1.60	1.59	86.16
	Soluble	2.61	0.38	0.46	16.02
	Total	14.33	1.71	3.10	87.12
Ni	Insoluble	1.84	0.30	0.41	12.43
	Soluble	1.35	0.15	0.15	7.43
	Total	3.20	0.37	0.77	13.21
Pb	Insoluble	4.08	0.58	0.64	25.84
	Soluble	1.33	0.11	0.17	9.95
	Total	5.41	0.64	0.94	27.72
V	Insoluble	7.26	0.98	1.56	72.92
	Soluble	2.02	0.17	1.15	4.40
	Total	9.30	1.09	3.12	74.49

The metals Al and Fe and ions SO_4^{2-} and NO_3 presented the highest concentrations at both sites. Al and Fe values in rainwater collected at the RV site show that these metals are probably crustal. The RV site has a complex orography; there is frequent turbulence lasting 1–2 h several times during the day. The site has no industrial emission sources; pollutants reaching the site that could contribute to high metal contents in rainwater are transported by air from industrial zones in Toluca and Mexico City.

The Spearman rank order correlation was applied to trace metal concentrations (insoluble and soluble fractions) and to all major inorganic ions. Matrix correlations are shown in Tables 3a and 3b. Significant values are indicated by bold type. In general, there is a strong positive correlation among all the elements (Table 3a). For the Rancho Viejo data, there is strong correlation between Al and Cd, Cr, Mn, Ni, Pb and V. Table 3b shows the correlations of Al with Cr, Fe, Mn, Ni, Pb and V corresponding to the Mexico City samples. The remaining trace metal concentrations in the soluble fractions do not show strong correlations.

A high correlation between Al and Mn is associated with electroplating and smelter activities in industrial zones, although Mn also receives a contribution from crustal material, as some authors [16,17] have pointed out.

Halstead et al., 2000 [18], found that Cd, Cu, Pb and Zn were enriched in rainwater relative to crustal material and they suggest a significant anthropogenic contribution for these elements. Although correlations among species are frequently used to make inferences about the sources of pollutants, it is necessary to be cautious in the interpretation of correlation coefficients in rainwater data, because the concentration may vary according to scavenging from the atmosphere, particle sizes and hydroscopic properties of particles [19].

3.2. *Statistical factor analysis*

To assess relationships between concentrations of the elements studied, factor analysis (principal component analysis) and Pearson's correlation were applied. In Tables 4a and 4b the factor loadings normalised by the Varimax extraction are shown. The Varimax extraction aims to maximise the variances of the squared normalised factor loadings across variables for each factor to make the interpretation easier. This is the most-used method [20]. Five factor groups were identified. The factors accounted for 62.59% (Rancho Viejo) and 50.43% (Mexico City) of the total variance.

For Rancho Viejo, the first factor explained 30.83% of the total variance, with high loadings on NH_4^+, Ca^{2+}, Na^+ and NO_3^-, and moderate loadings on SO_4^{2-}, Mg^{2+} and Fe in the insoluble fraction. This factor indicates a soil crustal contribution for NH_4^+ Ca^{2+}, Na^+, Mg^{2+}, with a significant crustal source for Fe, but mainly anthropogenic, as indicated by the enrichment factors. The loadings on SO_4^{2-} suggest that these ions come from anthropogenic sources through their precursor SO_2. These ions are significantly correlated; their concentrations in rainwater varied in the same manner. The second factor indicates high loading on Al, Pb, Cr, V, Ni and Mn and a low loading on Cd in the insoluble fraction, and explains 10.64% of the total variance. This factor suggests a possible anthropogenic contribution but a significant crustal contribution for Al. Although Cd has a small loading, the high value found in the crustal enrichment factors (EF_{crust}s) indicates an important contribution from anthropogenic sources.

The first factor for Mexico City can be considered to represent an anthropogenic origin, since Pb, Cr, Mn, V and Ni, which mostly originate from anthropogenic sources, are the major components of this group. This is seen by the high values found in the EF_{crust}s. This factor accounted for 20.12% of the total variance. The inclusion of Al and Fe in this first factor suggests that these metals were emitted from anthropogenic sources such as combustion processes, metallurgic industries, and smelters [7,21]. The second factor explained 10.43% of the total variance, with high loadings

Table 3a. Spearman Rank Order correlations among all trace metals (insoluble fraction) and inorganic ions in rainwater at Rancho Viejo, 2003–2004. Bold numbers are significant at $p < 0.05$ ($N = 51$).

	Al	Cd	Cr	Fe	Mn	Ni	Pb	V	SO_4^{2-}	Cl^-	NO_3^-	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	pH
Al	1.00																
Cd	**0.74**	1.00															
Cr	**0.79**	**0.70**	1.00														
Fe	0.28	0.15	0.28	1.00													
Mn	**0.63**	**0.62**	**0.61**	0.34	1.00												
Ni	**0.71**	**0.62**	**0.82**	0.28	**0.56**	1.00											
Pb	**0.75**	**0.69**	**0.64**	0.39	**0.62**	**0.58**	1.00										
V	**0.76**	**0.62**	**0.73**	0.37	**0.70**	**0.64**	**0.80**	1.00									
SO_4^{2-}	0.19	0.28	0.19	0.16	0.19	0.23	0.21	0.21	1.00								
Cl^-	−0.09	0.13	0.08	0.05	0.004	0.08	0.06	0.03	0.49	1.00							
NO_3^-	0.27	0.36	0.24	0.39	0.31	0.24	0.25	0.18	**0.60**	0.29	1.00						
NH_4^+	0.09	−0.12	0.13	**0.56**	0.13	0.18	0.11	0.12	**0.53**	0.17	**0.77**	1.00					
Na^+	0.29	−0.07	0.22	0.16	**0.64**	0.22	0.23	0.16	0.38	0.38	**0.63**	**0.72**	1.00				
K^+	0.16	0.29	0.25	0.40	0.13	0.33	0.14	0.14	0.20	0.22	0.30	0.23	0.33	1.00			
Ca^{2+}	0.22	0.15	0.14	**0.69**	0.25	0.17	0.18	0.11	0.32	0.03	**0.71**	**0.72**	**0.79**	0.43	1.00		
Mg^+	0.09	0.06	0.13	**0.56**	0.13	0.18	0.25	0.25	0.49	0.19	**0.63**	**0.54**	**0.63**	**0.75**	**0.75**	1.00	
pH	0.25	−0.03	0.05	0.13	0.06	0.12	0.18	0.17	0.01	0.03	−0.01	0.02	0.07	0.01	0.01	−0.02	1.00

Table 3b. Spearman Rank Order correlations among all trace metals (insoluble fraction) and inorganic ions in rainwater at Mexico City, 2003–2004. Bold numbers are significant at $p < 0.05$ ($N = 107$).

	Al	Cd	Cr	Fe	Mn	Ni	Pb	V	SO_4^{2-}	Cl^-	NO_3^-	NH_4^+	Na^+	K^+	Ca^{2+}	Mg^{2+}	pH
Al	1.00																
Cd	−0.09	1.00															
Cr	**0.69**	−0.13	1.00														
Fe	**0.61**	−0.09	**0.62**	1.00													
Mn	**0.52**	0.12	**0.53**	**0.60**	1.00												
Ni	**0.64**	−0.07	**0.55**	**0.55**	**0.57**	1.00											
Pb	**0.74**	−0.17	**0.67**	**0.67**	**0.50**	0.46	1.00										
V	**0.66**	−0.23	**0.60**	**0.63**	0.47	0.39	**0.68**	1.00									
SO_4^{2-}	0.25	0.08	0.15	0.22	0.03	0.13	0.19	0.07	1.00								
Cl^-	0.12	0.008	0.04	0.14	0.06	0.17	0.14	0.02	0.43	1.00							
NO_3^-	0.27	0.11	0.19	0.28	0.11	0.20	0.20	0.13	**0.69**	**0.54**	1.00						
NH_4^+	0.37	0.17	0.23	0.28	0.17	0.26	0.28	0.13	**0.75**	0.49	**0.78**	1.00					
Na^+	0.35	0.11	0.23	0.27	0.29	0.37	0.32	0.13	**0.54**	0.45	0.48	**0.89**	1.00				
K^+	0.39	0.13	0.28	0.31	0.27	0.34	0.37	0.17	**0.57**	0.44	0.47	**0.68**	**0.89**	1.00			
Ca^{2+}	0.34	0.12	0.15	0.29	0.18	0.30	0.32	0.14	**0.69**	0.48	**0.64**	**0.81**	**0.84**	**0.79**	1.00		
Mg^+	0.32	0.12	0.16	0.30	0.18	0.28	0.32	0.16	**0.71**	**0.50**	**0.64**	**0.79**	**0.86**	**0.83**	**0.97**	1.00	
pH	0.20	−0.02	0.11	0.20	0.23	0.21	0.20	0.14	0.01	0.03	−0.01	0.02	0.07	0.01	0.01	−0.02	1.00

Table 4a. Factor loading with varimax-normalised extraction among all trace metals (insoluble and soluble fractions) and inorganic ions in rainwater at Rancho Viejo, 2003–2004.

Elements	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Al (insol)	0.20	**0.83**	−0.16	0.01	0.25
Cd (insol)	−0.10	**0.62**	0.05	−0.16	−0.18
Cr (insol)	0.37	**0.80**	0.10	0.24	−0.05
Fe (insol)	**0.69**	0.39	−0.22	0.08	−0.08
Mn (insol)	0.46	**0.71**	0.09	0.20	−0.02
Ni (insol)	0.15	**0.76**	−0.005	0.14	0.03
Pb (insol)	0.19	**0.83**	−0.14	−0.13	0.005
V (insol)	0.43	**0.77**	0.02	0.26	0.05
Al (sol)	−0.03	0.10	−0.12	**0.58**	0.09
Cd (sol)	0.13	−0.09	−0.58	−0.27	−0.18
Cr (sol)	−0.21	0.15	0.13	−0.28	0.45
Fe (sol)	0.24	−0.05	**0.63**	−0.16	0.19
Mn (sol)	0.11	−0.29	0.47	0.10	0.39
Ni (sol)	0.04	0.30	0.13	−0.49	−0.14
Pb (sol)	0.244	−0.19	−0.46	0.34	−0.12
V (sol)	−0.17	−0.06	−0.04	−0.02	−0.52
SO_4^{2-}	**0.58**	0.24	0.26	0.27	−0.06
Cl^-	0.34	0.11	0.17	**0.57**	0.01
NO_3^-	**0.76**	0.12	0.04	−0.02	0.11
Na^+	**0.82**	0.28	0.008	0.17	0.18
K^+	0.15	0.22	0.20	**0.78**	−0.25
Ca^{2+}	**0.86**	−0.01	−0.10	−0.004	−0.46
Mg^{2+}	**0.66**	0.37	0.11	0.50	−0.20
NH_4^+	**0.89**	0.22	0.02	−0.01	0.02
pH	0.02	0.17	−0.65	0.11	0.43
% Total variance	30.83	10.64	7.82	7.56	5.74

Note: Main components (bold numbers are significant at > 0.5).

Table 4b. Factor loading with varimax-normalised extraction among all trace metals (insoluble and soluble fractions) and inorganic ions in rainwater at Mexico City, 2003–2004.

Elements	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
Al (insol)	**0.82**	0.14	0.06	−0.05	0.15
Cd (insol)	−0.07	−0.07	**0.73**	−0.11	−0.13
Cr (insol)	**0.76**	−0.004	−0.17	0.17	0.05
Fe (insol)	**0.83**	0.10	−0.005	0.13	−0.13
Mn (insol)	**0.74**	0.049	0.064	−0.17	−0.12
Ni (insol)	**0.64**	0.22	0.05	−0.20	−0.08
Pb (insol)	**0.77**	0.08	−0.09	0.16	0.008
V (insol)	**0.68**	0.04	−0.10	0.10	0.35
Al (sol)	0.14	−0.16	0.25	**0.54**	0.04
Cd (sol)	0.01	0.29	−0.15	−0.12	0.21
Cr (sol)	−0.08	0.12	−0.02	0.08	**0.52**
Fe (sol)	0.11	0.35	−0.04	**0.59**	0.02
Mn (sol)	0.19	0.09	−0.22	0.47	−0.32
Ni (sol)	0.26	0.01	**0.61**	0.12	0.31
Pb (sol)	0.13	0.02	0.18	−0.29	0.26
V (sol)	0.28	0.02	0.02	−0.01	**0.58**
SO_4^{2-}	−0.05	**0.77**	0.10	0.08	0.23
Cl^-	0.05	0.29	0.27	0.09	−0.41
NO_3^-	0.04	**0.78**	0.02	0.07	0.07
Na^+	−0.11	0.08	**0.54**	−0.16	0.01
K^+	0.19	**0.76**	−0.05	0.05	−0.22
Ca^{2+}	−0.10	−0.001	−0.09	**0.56**	0.16
Mg^{2+}	0.35	**0.78**	0.12	0.12	−0.18
NH_4^+	0.15	**0.51**	−0.37	−0.25	0.06
pH	0.28	0.009	−0.26	−0.20	−0.37
% Total variance	20.12	10.43	7.40	6.36	6.12

Note: Main components (bold numbers are significant at $p > 0.5$).

on NO_3^-, Mg^{2+}, SO_4^2 and K^+ and a low loading on NH_4^+. This factor indicates a crustal soil contribution for Mg^{2+} and K^+. The loadings on NO_3^-, SO_4^{2-} and NH_4^+ suggest that these ions come from anthropogenic sources through their precursors SO_2 and NO_x. The loadings on Mg^{2+} and NH_4^+ suggest that neutralisation reactions occurred.

3.3. *Enrichment of metals*

Crustal enrichment factors (EF_{crust}s) were calculated for each element and the values compared to the relative crustal abundance of the respective element in order to evaluate the contribution of non-crustal sources in rainwater samples.

EF_{crust}s were calculated using the following equation [17]:

$$EF_{crust} = \frac{(C_x/C_{Ca})_{sample}}{(C_x/C_{Ca})_{crust}},$$

where $(C_x/C_{Ca})_{sample}$ is the ratio of the concentrations of element X and Ca in the rainwater sample and $(C_x/C_{Ca})_{crust}$ is the concentration of the same element with respect to crustal material. The EF_{crust}s were calculated using average concentrations of crustal elements from Mason (1966)

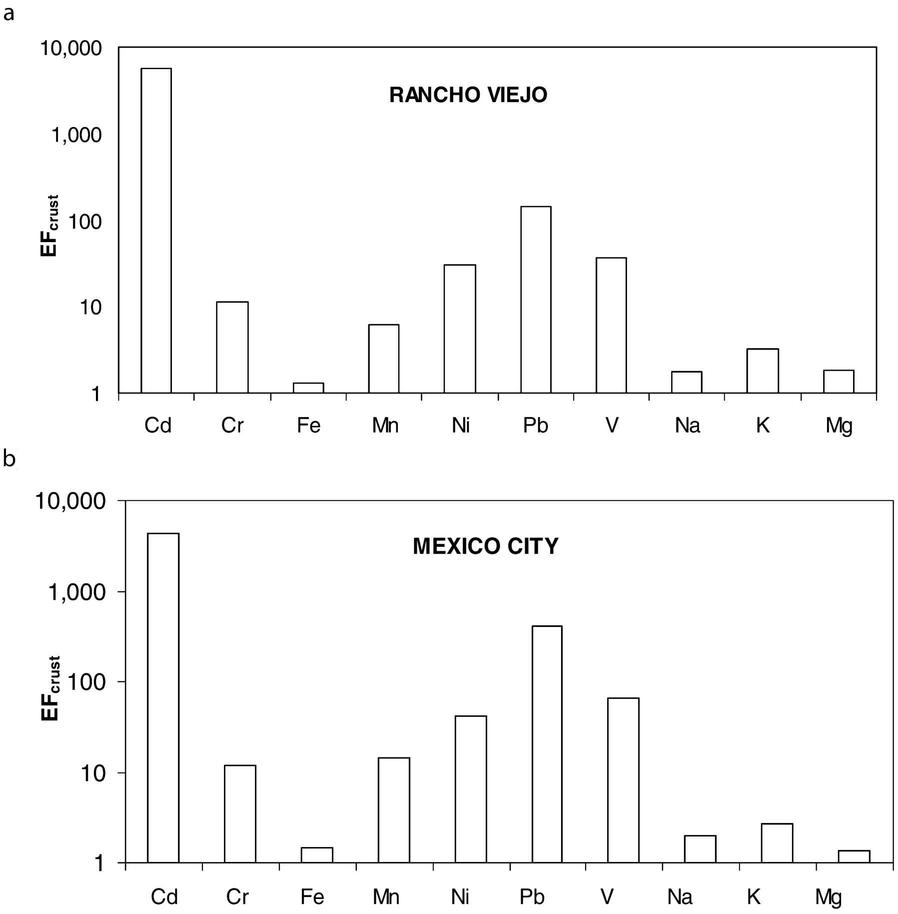

Figure 2. a: Average enrichment factors for Cd, Cr, Fe, Mn, Ni, Pb, V, Na^+, K^+, and Mg^{2+} for RV. b: Average enrichment factors for Cd, Cr, Fe, Mn, Ni, Pb, V, Na^+, K^+, and Mg^{2+} for CU.

and the average EF_{crust}s of elements in rainwater (Figure 2). For trace metals, the soluble plus insoluble rainwater fractions were used.

By convention, an arbitrary average EF_{crust} value <10 was chosen to indicate that an element in rainwater has a significant crustal source. This element is referred to as a non-enriched element (NEE). If an average EF_{crust} value is >10, a significant proportion of the element is considered to have a non-crustal source. This element is referred to as an anomalously enriched element (AEE).

Aluminium, Fe, Na^+, K^+ and Mg^{2+} cations were considered to be NEE. From both sample sites, Cadmium, Pb, V, Ni, Mn and Cr, in decreasing order, presented EF_{crust} values >10 and are considered AEE, indicating a non-crustal source. In general, Pb, V, Ni, Mn and Cr are associated with fine particles ($<1\,\mu m$), which are generated as high–temperature combustion condensates and emitted to the boundary layer by smoke-stacks [8].

EF_{crust}s are based on a ‘standard crust composition’ and must therefore be interpreted with caution in areas where the chemical composition of dust particles differs from the standard crust. In this case, as far as we know, there are no anthropogenic sources in Mexico City that could raise the sodium ion enrichment factor to the values calculated in this study. Obviously, sea spray is ruled out as a source because the distance to the coast is more than 800 km and Mexico City is surrounded by high mountains. Al-Momani et al. (2002) [24] have also stated that there is uncertainty in defining the composition of crustal source material. Kaya and Tuncel (1997), Kim et al. (2000) and Halstead et al. (2000) [16–18] found crustal material enriched by Cd, Cu, Pb, and Zn in rainwater, indicating a significant anthropogenic contribution.

3.4. *Back trajectory analysis*

The VWMC (volume weighted mean concentration) of major ions and trace metals in rainwater and the number of samples for each sector are shown in Tables 5a, 5b, 6a and 6b. The relationships to wind directions obtained by air mass back trajectory analysis are also presented. The individual concentrations of SO_4^{2-} (as a chemical tracer of anthropogenic pollution), of Ca^{2+} (as chemical tracers of crustal particles), and of trace metals were associated with the corresponding air mass back trajectories calculated for 2003 and 2004 by the NOAA HYSPLIT model (hybrid single-particle lagrangian integrated trajectory model) [25]. The 1000 MAGL (metres above ground level) was used because storm cloud bases frequently lie around 1000 MAGL. The 3000 MAGL is about 1200 m higher than the highest mountain summit lying between Mexico City and Toluca and Rancho Viejo; it is also close to the height of the 500 millibar (mb) isobaric surface (one of the mandatory levels in meteorological analysis). The back trajectories in the RV site were grouped into three wind direction sectors: sector 1 from 1° to 90°; sector 2 from 91° to 135°; and sector 3 from 136° to 360°. The criteria for defining these sectors in the study of rainwater chemical composition at the RV site were based on the geographical direction of large urban and industrial areas in relation to this site, and on the direction of prevailing winds during the rainy season. Since the MC site is surrounded by intense anthropogenic emission sources, the air mass back trajectory sectors were subdivided into four equal sectors; that is, 1 to 90, 90 to 180, 180 to 270 and 270 to 360 degrees. Figures 3a and 3b show an example of four trajectories chosen at random because it is not convenient to show the 158 trajectories in this paper. Tables 5a, 5b, 6a and 6b show the observed variability in ions and trace metals by sector corresponding to the 1000 and 3000 MAGL trajectories.

At the RV site, volume-weighted mean SO_4^{2-} concentrations (Table 5a) were higher when air mass back trajectories at 1000 MAGL came from 1° to 90° ($44.34\,\mu eq\,l^{-1}$) and from 91°–135° ($56.25\,\mu eq\,l^{-1}$) compared to trajectories in the 136°–360° sector ($15.96\,\mu eq\,l^{-1}$). The higher VWMC of sulfate observed when the wind direction came from the sector is evidence of the interchange of air mentioned above. A similar result was obtained for NH_4^+, although the difference between concentrations for sectors 2 and 3 was much less (40.97, 25.79 and 20.86 μeq l^{-1} for sectors 1, 2, 3, respectively).

At the MC site, NH_4^+ was the most abundant ion in all four sectors in both back trajectories, followed by SO_4^{2-}. The low sample number obtained in sectors 3 and 4 agrees with the synoptic meteorological conditions that prevail in Central Mexico during the rainy season; trade winds have a consistent component from the east; that is, winds are from between the north and southeast most of the time during this season. Calcium in rainwater samples comes from wind-blown dust particles from sedimentary soils northeast of Mexico City. These particles neutralise acids in rainwater, as suggested by the concentrations of H^+ and Ca^{2+}, which clearly indicate a neutralisation process. For example, at the MC site at 1000 MAGL, the highest concentration of Ca^{2+} was observed for sector 2 (47.63 μeq l^{-1}). Similar results were observed at 3000 MAGL (see Table 6a). There was also reasonably good correspondence with the physical characteristics of the areas located in the different sectors. It is nevertheless interesting to note that the lowest concentrations of Ca^{2+} observed at both levels for sector 3 (23.47 μeq l^{-1}) are consistent with wooded areas (which partially impede dust particles from being blown by winds) predominating south to west of the MC site, and the highest concentrations of this ion observed at both levels for sector 2 are consistent

Table 5a. Volume weighted mean concentrations of major ions (μeq l^{-1}) for four wind direction sectors in rainwater collected at the Rancho Viejo in 2003 and 2004.

	Air mass trajectory sector at 1000 m AGL†			Air mass trajectory sector at 3000 m AGL†		
Ion	N-E Sector 1 1°–90°	E-S Sector 2 91°–135°	S-W Sector 3 136°–360°	N-E Sector 1 1°–90°	E-S Sector 2 91°–135°	S-W Sector 3 136°–360°
N	36	2	13	35	2	14
SO_4^{2-}	44.34	56.25	15.96	64.45	45.10	34.34
Cl^-	7.00	5.21	47.76	6.97	6.33	4.84
NO_3^-	25.92	24.29	29.51	25.82	28.58	28.88
Na^+	1.54	2.39	1.25	1.55	1.84	1.31
K^+	5.72	6.76	3.35	5.62	5.58	3.59
Ca^{2+}	7.78	13.37	6.70	8.58	12.60	7.00
Mg^{2+}	2.19	3.44	1.65	2.17	3.52	1.71
NH_4^+	40.97	25.70	20.86	40.81	47.14	32.60

Notes: N = sample number.
†Metres above ground level.

Table 5b. Volume weighted mean concentrations of trace metals (soluble + insoluble fractions) in μg l^{-1} for four wind direction sectors in rainwater collected at the Rancho Viejo in 2003 and 2004.

	Air mass trajectory sector at 1000 m AGL†			Air mass trajectory sector at 3000 m AGL†		
Metal	N-E Sector 1 1°–90°	E-S Sector 2 90°–180°	S-W Sector 3 180°–270°	N-E Sector 1 1°–90°	E-S Sector 2 90°–180°	S-W Sector 3 180°–270°
N	32	3	16	34	5	12
Al	117.28	100.47	105.70	117.33	92.10	107.97
Cd	1.31	0.66	1.01	1.28	1.036	0.94
Cr	1.66	1.58	1.46	1.64	1.42	1.52
Fe	117.38	111.19	88.85	114.11	117.11	87.00
Mn	8.15	8.16	7.33	8.19	7.45	7.26
Ni	2.47	1.93	3.02	2.41	2.15	3.37
Pb	3.35	1.71	2.68	3.20	2.55	2.79
V	5.71	5.80	6.97	5.66	8.22	6.50

Notes: N = sample number.
†Metres above ground level.

Table 6a. Volume weighted mean concentrations of major ions (μeq l^{-1}) for four wind direction sectors in rainwater collected at the University of Mexico in 2003 and 2004.

	Air mass trajectory sector at 1000 m AGL†				Air mass trajectory sector at 3000 m AGL†			
Ion	N-E Sector 1 1°–90°	E-S Sector 2 90°–180°	S-W Sector 3 180°–270°	W-N Sector 4 270°–360°	N-E Sector 1 1°–90°	E-S Sector 2 90°–180°	S-W Sector 3 180°–270°	W-N Sector 4 270°–360°
N	34	46	9	18	26	58	9	14
SO_4^{2-}	60.11	54.89	62.03	67.23	65.48	54.63	75.46	56.17
Cl^-	10.48	10.00	13.02	9.65	11.97	9.67	11.64	9.31
NO_3^-	55.94	54.19	70.81	49.06	63.45	53.49	61.36	43.63
Na^+	6.07	5.10	7.18	4.59	6.88	5.29	4.10	4.70
K^+	2.39	2.30	3.00	1.78	2.50	2.39	2.12	1.64
Ca^{2+}	40.70	47.63	23.47	33.61	33.79	41.70	23.78	32.64
Mg^{2+}	4.15	3.73	4.85	3.22	4.79	3.73	3.21	3.16
NH_4^+	109.91	112.77	105.49	97.02	105.70	117.22	100.87	89.13

Notes: N = sample number
†Metres above ground level.

Table 6b. Volume weighted mean concentrations of trace metals (soluble + insoluble fractions) in μg l^{-1} for four wind direction sectors in rainwater collected at the University of Mexico in 2003 and 2004.

	Air mass trajectory sector at 1000 m AGL†				Air mass trajectory sector at 3000 m AGL†			
Metal	N-E Sector 1 1°–90°	E-S Sector 2 90°–180°	S-W Sector 3 180°–270°	W-N Sector 4 270°–360°	N-E Sector 1 1°–90°	E-S Sector 2 90°–180°	S-W Sector 3 180°–270°	W-N Sector 4 270°–360°
N	36	49	9	13	29	55	7	16
Al	166.75	150.43	144.79	86.12	164.45	154.48	131.22	100.80
Cd	0.41	0.65	0.48	0.38	0.43	0.61	0.36	0.43
Cr	1.30	1.12	1.34	1.08	1.27	1.16	1.43	1.07
Fe	168.14	154.77	130.10	88.66	183.57	148.78	127.14	98.26
Mn	16.31	14.17	14.06	16.31	17.31	14.06	14.20	16.47
Ni	3.35	2.62	2.35	3.69	3.49	2.61	2.13	3.67
Pb	5.03	5.67	7.51	7.14	5.38	5.36	6.65	7.63
V	6.98	5.24	6.63	7.75	7.18	5.38	7.26	7.08

Notes: N = sample number.
†Metres above ground level.

with industrial areas being situated between northwest and northeast of the MC site, although some wooded areas also lie west to the northwest of the MC site. It is important to mention that Ca^{2+} is mobilised in wooded areas by means of winds that transport Ca^{2+} particles from deforested, eroded zones.

Of the trace metals analysed, Al was the most abundant in all sectors, followed by Fe, Mn, V, Pb and Ni. Concentrations were not clearly related to wind direction, as may be observed in Tables 5b and 6b. This result was unexpected because most of the trace metal sources – and surprisingly, the air mass back trajectory analysis for both levels – showed that only the highest concentrations of the metals Mn, Pb and V were observed when winds blew from sectors 1 and 2, where most of the urban and industrial pollution sources lie. The highest concentrations of Mn were observed for sector 1 at 3000 MAGL. The analysis at 3000 MAGL gave the expected results, the highest concentrations of Al being observed for sector 1, where large areas of bare soil lie. An attempt was made to associate trace metals and major ion concentrations with surface wind data obtained at two meteorological stations, however, the results did not coincide with what was expected, almost certainly because surface winds at the MC site tend to be variable and weak.

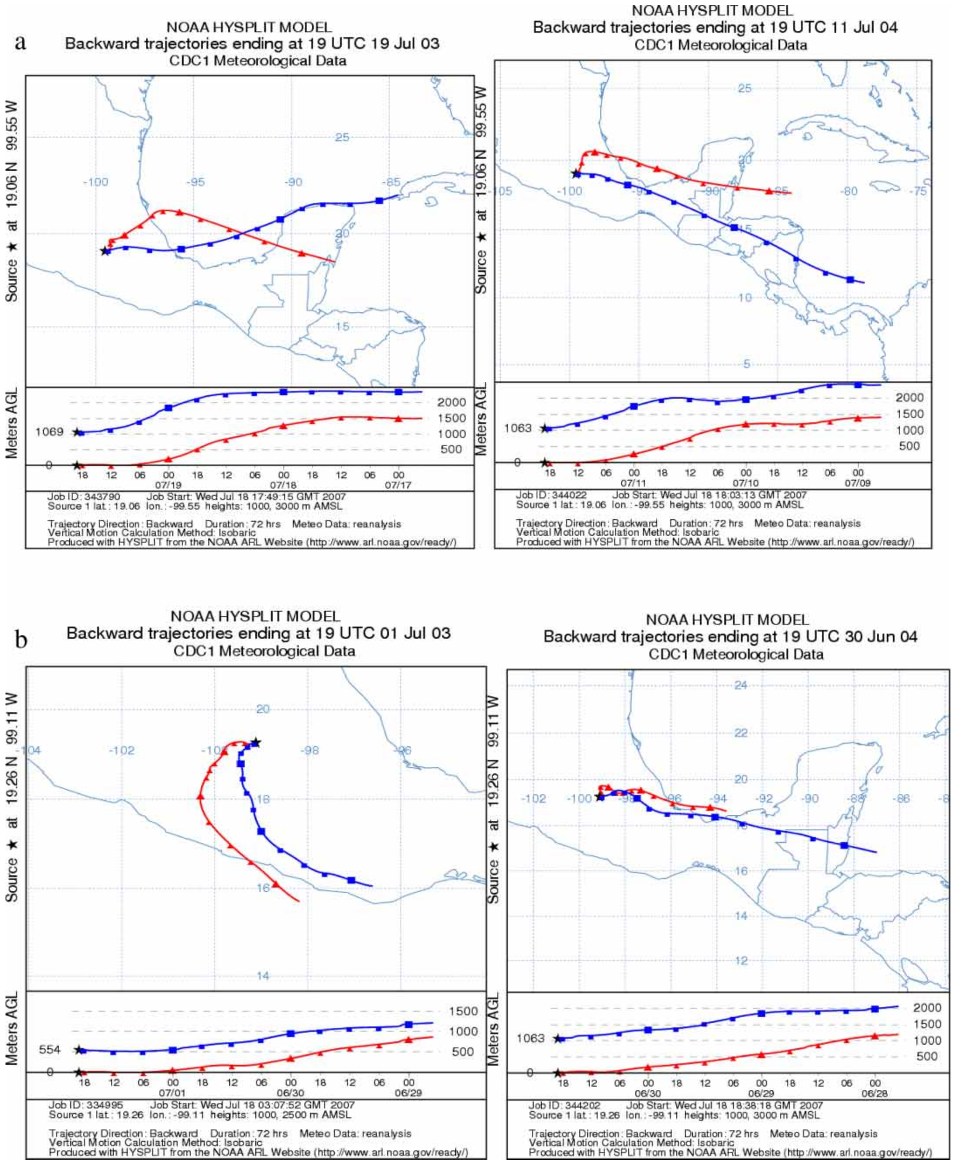

Figure 3. a: Air-mass back trajectories observed during the rainy season in 2003 and 2004 for RV corresponding to 1000 and 3000 MAGL. b: Air-mass back trajectories observed during the rainy season in 2003 and 2004 for CU corresponding to 1000 and 3000 MAGL.

3.5. *Solubility*

Acidity in precipitation depends mainly on the presence of H_2SO_4, HNO_3 and organic acids. The rains from the RV site were acid, with a mean pH (calculated from the H^+ concentration) of 4.92. Acidity in rain is neutralised mainly by (NH_4^+ and $CaCO_3$). The pH of rainwater depends on the relative abundance of acids and bases and of neutralisation reactions between them [23,24]. If H_2SO_4, HNO_3, NH_4^+ and $CaCO_3$ are the only species involved in acid precipitation, a linear relationship between (NO_3^- + SO_4^{2-}) and (H^+ + Ca^{2+} + NH_4^+) is expected. This relationship is shown in Figure 4. The correlation coefficient between variables is 0.836, indicating that the acidity

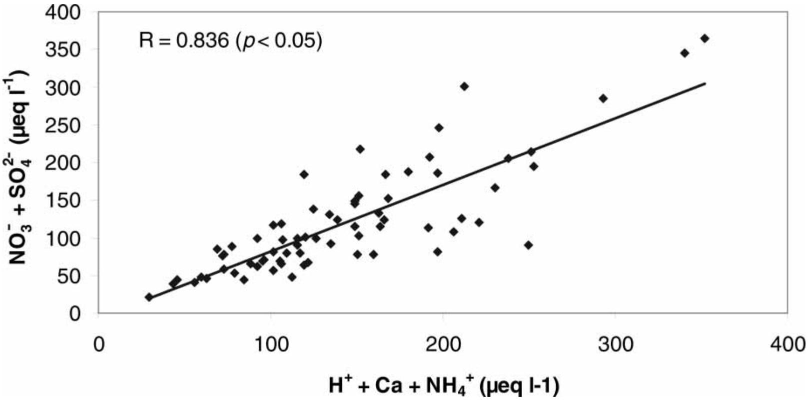

Figure 4. Linear regression of $(NO_3^- + SO_4^{2-})$ vs. $(H^+ + Ca^{2+} + NH_4^+)$.

is caused by H_2SO_4 and HNO_3 and neutralised mainly by NH_4^+ and $CaCO_3$. These results indicate a greater relationship between H^+ and SO_4^2 and NO_3^- ions at the RV site because neutralisation reactions between soil particles and acids in rainwater are less important at this location than at the MC site. The high rainwater acidity observed at the RV site shows the large impact of Mexico City emissions on air and rainwater quality in downwind wooded areas, with possible acidification of the forest soil.

4. Conclusions

The large variations in the chemical composition of rainwater observed at both sampling sites occurred due to the complex topography of the Mexico City valley and surrounding areas. This may produce inconsistencies when relating ionic and trace metal concentrations in rainwater to the air mass back trajectory analysis. A detailed analysis of wind flow patterns based on reliable soundings at various altitudes above ground level in different zones of the Mexico City valley is needed to provide a better high-resolution air mass back trajectory analysis (wind patterns). High concentrations of Cd, Mn, Pb and V were found at the RV and MC sites sampled during the period 2003–2004. Trace metals were emitted mainly by anthropogenic sources. This was supported by EF_c factor values, which showed a non-crustal source for these metals. Aluminium and Fe presented the highest concentrations in the soluble and insoluble fractions, indicating that a significant quantity of these metals had a crustal or geological origin.

The application of factor analysis (principal component analysis) gave a clear indication of the anthropogenic and natural origins of the trace metals. However, the sources may also be related to human activities; combustion of a large amount of fossil fuel. Non-labile species are significantly predominant in the rain, which may be due to dusty conditions and poor vegetation. The results of metal loading may indicate an association with variations in deposition velocities, emission sources and meteorological conditions (i.e. wind direction, wind speed, atmospheric stability).

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