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Chemical composition of bulk precipitation in the metropolitan area of Costa Rica, Central America

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ABSTRACT

Trace metals and inorganic ions were measured in bulk precipitation sampled at eleven sites in the metropolitan area of Costa Rica. The ions were analyzed by ion chromatography, and the trace metals by atomic absorption spectrometer with a graphite furnace attachment. The results indicated that Na^+ and SO_4^{2-} were the most abundant ions, and of the metals, that Al and Fe had the highest concentrations.

Spearman's correlation applied to all data showed a high correlation among SO_4^{2-}, NO_3^- and NH_4^+, indicating a common anthropogenic origin. In addition, the correlation found between Na^+, K^+ and Cl^- indicated a sea aerosol contribution. High positive correlations between trace metals were found for Al–Mn, Ni–Mn, Ni–Al, Cu–Ni, Pb–Cu, Pb–Ni and Pb–Mn.

1. Introduction

Bulk precipitation is defined as the amount of wet precipitation plus dry particles that sediment during sampling into the collector located in an air environment. However in practice, this amount may be affected by the simultaneous precipitation of fine particles and gases. Because of this, total precipitation is often defined operationally as total material deposition in a continuously open sampler. Whichever definition is used, however, 'bulk' deposition into a sampler forms only part of the total deposition to the surrounding ecosystem, because due to turbulent deposition of gases and fine particles, total deposition onto vegetative surfaces generally exceeds deposition onto the surfaces of 'bulk' samplers.

Precipitation chemistry is the result of complex interactions between the dynamics of clouds and microphysical processes, as well as a series of atmospheric chemical reactions that occur in the interior of and below the clouds. Acidity and ion concentration in the precipitate depend on the intensity of constituent sources, their incorporation into the system, physical and chemical transformation during the process of cloud formation and drag below the cloud (Kulshrestha et al., 1999).

Potentially toxic metals, notably Cu, Cr, Ni and Pb (Galloway et al., 1982a,b), have been mobilized in the environment by industrialization, especially high temperature processes such as non-ferrous metal smelting, fossil fuel combustion vehicle exhaust, and other human activities, and stay there until they are removed by a variety of cleansing processes including dry deposition, scavenging and washout by rain (Hamilton-Taylor and Willis, 1990). Heavy metals emitted by combustion processes usually have relatively high solubilities and reactivities, because of the small sizes of particles on which they are carried. Thus, they dissolve readily in rain, especially under low pH conditions, resulting in polluted rainwater (Salomons, 1996).

The 51,100 km^2 area that comprises the territory of Costa Rica has a wide geographical and climatic diversity with ridges bearing abundant rich volcanic cones. These ridges cross the country from NW to SE, with a maximum height of around 4000 m, forming a central plateau of approximately 3000 km^2, known as the metropolitan area. Its average elevation is 1100 m, and it contains some 75% of the country's

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vehicle fleet (approximately 734,200 units), 65% of domestic industry and 60% of Costa Rica's population (2,580,000, according to data from the last population census conducted in 2000) (INEC, 2000). As a result of the lack of efficient urban planning, the expansion of the metropolitan area during the last 20 years has produced a marked degradation of air quality, exposing the population to an annual average PM_{10} concentration of approximately 46 μg m^{-3} and annual averages of nitrogen dioxide between 64 and 81 μg m^{-3} in the high traffic areas of this region (Herrera and Rodríguez, 2007).

Atmospheric precipitation is one of the most effective natural mechanisms for removing gaseous and particulate pollutants in the atmosphere. It is therefore important to determine the composition of chemical precipitation in order to predict the potential impact of its incorporation into the ecosystems.

This study aims to describe the bulk precipitation in Costa Rica, a tropical country, identifying the contribution of inorganic species (larger cations and anions and trace metals) in samples of atmospheric precipitation in order to estimate the main anthropogenic sources responsible for the contamination in the area. This is the first study of this kind developed in

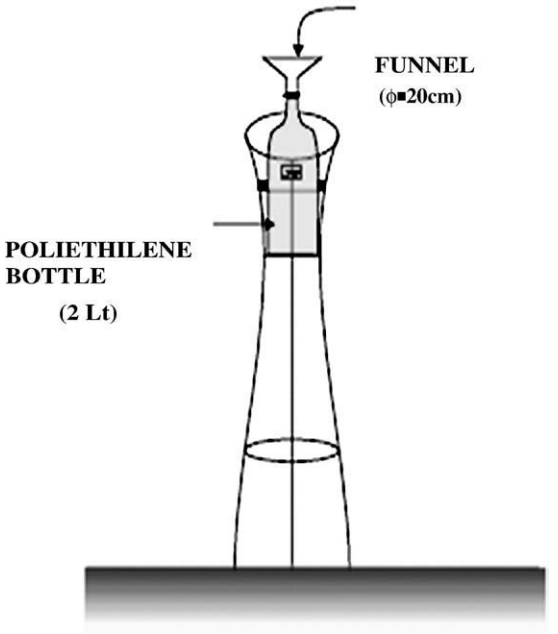

Fig. 2. Device used for collecting bulk precipitation samples.

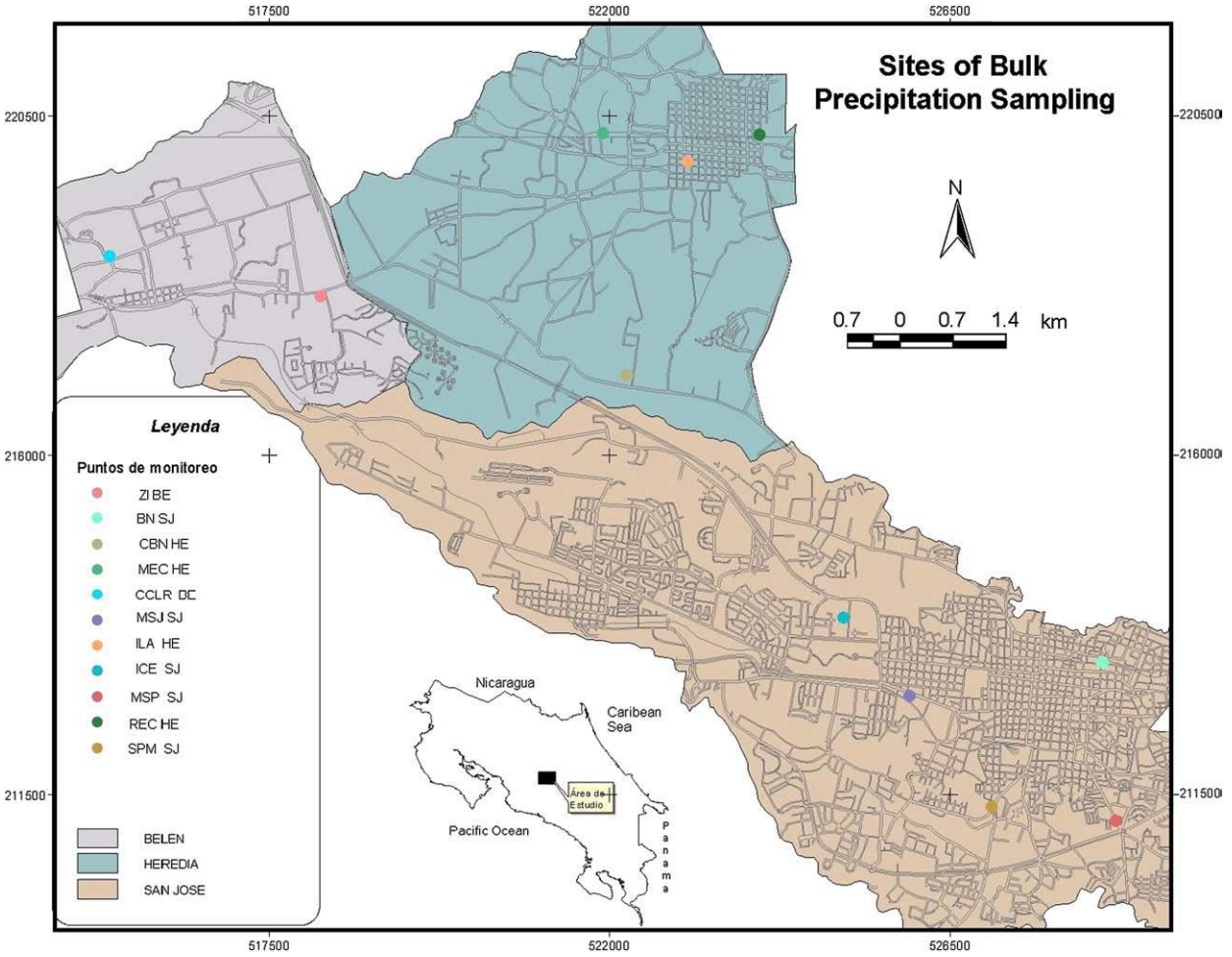

Fig. 1. Location of sampling sites for bulk precipitation in the Metropolitan Area of Costa Rica.

Table 1
Instrumental conditions used to determine ionic species present in collected samples of bulk precipitation.

	Anions	Cation
Detector	Electrical conductivity attached to suppresor	Electrical conductivity attached to suppresor
Column	Dionex IonPac AS9-HC Particle size: 9 μm (2×250 mm)	Dionex IonPac CS12A Particle size: 9 μm (2×250 mm)
Electrolytic suppresor	Dionex ASRS ULTRA II	Dionex CSRS ULTRA II
Mobile phase	Na_2CO_3 dissolution 9 mM to pH = 10.88	Dissolution of methasulphonic acid 20 mM
Injection volume	10 μl	10 μl
Mobile phase flow	0.25 ml/min	0.25 ml/min
Column temperature	30 °C	30 °C

Central America and will set a reference for future research in this region.

2. Experimental

2.1. Sampling

A total of 11 sampling sites located in three cities were selected: San Jose [flat roof of the National Library building (BN-SJ), Costa Rica Institute of Electricity building (ICE-SJ), Municipality of San Jose building (MSJ-SJ), Headquarters of the Ministry of Public Security of Costa Rica (MSP-SJ), Parks Section building of the Municipality of San Jose (SPM-SJ)], Heredia [(rectory of the National University building (REC-HE), Los Angeles Church (ILA-HE), Benjamin Nuñez Campus of the National University (CBN-HE), Mercedes Sur Recreation Park (MER-HE)] and Belen [La Ribera Commercial Center (CCLR-BE), Industrial Zone of Belen (ZI-BE)]. The geographical distribution of the sampling sites is shown in Fig. 1. At the selected sites, bulk precipitation was sampled by means of a funnel attached to a high-density polyethylene bottle through a hole in the lid, the space between the funnel and cap being filled with hot silicone to prevent contamination of the sample (Fig. 2). At each sampling site, two devices were placed to capture precipitation, one for ions and one for metals. For ion analysis, funnels and bottles were washed with deionized water (DW) between each sampling. For metals, after being washed with distilled water, the bottles were placed a minimum of 24 h in a bath of 10% nitric acid and then rinsed several times with DW. Sample collection during the campaign took place in periods 1–2 days long (depending on precipitation frequency), during the months of August–December, 2007. Collected volumes ranged from 20 to 95 ml. Containers were prepared for shipment of samples; ion analysis containers were rinsed with DW, and for heavy metals, bottles were rinsed with distilled water and left 24 h in an HNO_3 bath at 10%. Bottles were rinsed with distilled water and received three more rinses with DW.

2.2. Analytical procedures

2.2.1. Inorganic ions

Once the samples had been collected, they were transported to the laboratory. Sample volumes for ion analysis were measured with a graduated cylinder. Conductivity and pH were then measured using OAKTON equipment, model pH/CON 510, which allows the simultaneous measurement of both parameters. These measurements were made a maximum of 3 h after sample collection. A sample aliquot was then filtered through a Millipore 0.22 μm membrane, which was used for analysis of the main inorganic ions present. Samples were preserved at 4±2 °C, and ion quantification was performed within 48 h.

Ionic species were analyzed using microbore ion-exchange chromatography with suppression using a DIONEX ICS-3000 device, according to the conditions described in Table 1. Ionic species were identified and quantified by interpolation on a calibration curve of seven standard solutions and were prepared from certified commercial solutions MERCK Suprapur.

Standard solutions for the calibration curves were run every 10 analyzed samples, together with an intermediate solution for quality control prepared using a DIONEX certified synthetic sample to monitor response and reproducibility of peak height and retention times.

In addition, detection limits of ions were determined by taking 10 samples from different points and analyzing them using the same procedure as for the samples. Detection limits were calculated from the signal given by the concentration equal to the average of the signal, plus three times their standard deviation (Table 2).

2.2.2. Metals

For metal analysis, concentrated HNO_3 was added to pH<2 as a conservation mechanism. An aliquot of 25.00 ml of the sample was taken and poured into a 150 ml beaker, and 2.50 ml of concentrated HNO_3 added. The beakers were heated on a hot plate to almost dry. The remaining material was transferred quantitatively to a 25.00 ml volumetric flask. The extraction process was repeated once more. Once this process had been concluded, DW was added to the mark.

Metal analysis was carried out by atomic absorption spectrometry with a graphite furnace attachment using an AANALYST Perkin Elmer 700 spectrophotometer equipped with an auto sampler. A Perkin Elmer hollow cathode and deuterium lamps were used for the analysis of trace metals and background corrections respectively. Metal species were identified

Table 2
Detection limits and dynamic range for the determination of ionic species in bulk precipitation.

Ionic species	SO_4^{2-}	NO_3^-	Cl^-	PO_4^{3-}	F^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+
Detection limit (μeq/l)	2	3	11	20	3	2	0,8	2	6	2
Dynamic range (μeq/l)	5–208	4–161	7–282	8–316	13–526	4–348	3–205	5–399	8–658	6–444

Table 3
Volume weighted averages for the concentration of inorganic ions (μeq/l), conductivity (μS/cm) and metals (ug/l) found in bulk precipitation samples collected in eleven sampling sites located in the metropolitan area of Costa Rica, August–November, 2007.

Data	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	H^+	CE	V	Pb	Cr	Cu	Ni	Mn	Al	Fe
BN-SJ																	
N	25	25	25	25	19	15	19	25	25	15	24	21	25	17	25	25	25
Weighted average	9	3	61	15	20	8	16	15	15	4	5	4	4	3	16	354	58
Max value	40	8	115	42	51	14	70	52	74	5	7	5	10	3	32	620	88
Min value	2	0.8	21	2	5	2	9	2	4	2	3	2	3	2	7	127	32
Weighted *s*	8	1	28	0.4	15	4	31	13	14	0.6	1	0.8	2	0.4	6	116	14
MSP-SJ																	
N	37	37	37	37	28	12	15	37	37	29	35	33	37	32	37	37	37
Weighted average	8	4	56	10	12	6	8	37	18	2	3	2	4	2	20	324	54
Max value	25	30	176	18	36	10	32	126	42	3	8	5	13	4	43	485	88
Min value	2	0.8	5	3	5	4	4	1	5	2	1	1	1	1	7	158	28
Weighted *s*	6	5	27	5	3	3	31	27	8	0.5	2	1	3	1	8	72	14
SPM-SJ																	
N	36	36	36	36	23	17	15	36	36	32	36	34	36	33	36	36	36
Weighted average	6	3	48	13	8	10	7	25	13	2	4	3	5	2	20	322	52
Max value	15	11	140	27	73	19	35	85	39	4	7	6	10	3	32	456	72
Min value	1	1	14	9	3	5	4	2	4	1	1	2	2	1	11	229	27
Weighted *s*	3	2	25	14	16	6	12	22	6	0,8	2	1	1	0.4	6	56	11
MSJ-SJ																	
N	38	38	38	38	24	11	16	38	38	23	33	30	38	28	38	38	38
Weighted average	13	4	56	12	20	8	16	23	17	1	3	1	4	1	14	309	60
Max value	60	14	177	40	52	22	41	89	60	4	8	4	10	3	34	469	92
Min value	3	0.8	16	4	4	1	6	2	6	1	1	1	2	1	6	105	32
Weighted *s*	11	3	22	5	23	7	9	20	9	0.5	2	0.6	2	0.4	7	79	16
ICE-SJ																	
N	30	30	30	30	19			25	25	13	22	24	30	19	30	30	30
Weighted average	5	3	43	11	14	nd	nd	28	14	1.0	1	2	2	0.7	4	228	30
Max value	48	12	239	29	62			126	74	1.3	4	3	5	2	8	386	44
Min value	2	1	13	7	8			2	8	1.1	1	1	1.0	0.9	2	114	17
Weighted *s*	8	2	41	6	19			26	12	0.1	0.7	0.5	0.8	0.4	2	72	8
REC-HE																	
N	39	39	39	39	26	21	17	39	39	25	39	31	39	34	39	39	39
Weighted average	5	3	72	14	15	4	21	26	14	1	3	2	7	2	21	435	84
Max value	16	16	258	31	42	9	83	71	30	4	13	10	25	4	35	577	127
Min value	2	1	20	5	6	3	4	1	5	1	1	1	2	1	9	280	54
Weighted *s*	4	3	49	8	12	2	38	18	6	0.8	2	2	5	0.6	6	63	14
ILA-HE																	
N	37	37	37	37	21	16	18	37	37	32	37	34	37	27	38	38	38
Weighted average	14	3	55	10	22	7	21	14	14	2	3	3	5	0.9	22	468	77
Max value	53	10	153	34	49	12	55	71	55	3	8	7	8	3	51	574	105
Min value	1	1	12	3	4	4	6	0.8	4	1	2	1	2	1	9	294	49
Weighted *s*	11	2	26	7	8	3	10	15	9	0.5	2	1	2	0.5	9	76	15
MEC-HE																	
N	38	38	38	38	21			38	38	18	30	37	38	20	38	38	38
Weighted average	6	3	59	22	26	nd	nd	15	12	2	2	2	3	2	6	334	38
Max value	32	7	138	81	42			50	29	3	2	4	4	3.0	20	398	76
Min value	0.8	0.8	11	9	6			2	4	1	1	2	1	1.0	2	206	20
Weighted *s*	5	1	24	7	11			13	6	0.5	0.4	0.6	0.7	0.5	3	46	12
CBN-HE																	
N	18	18	18	18	16			18	18	17	18	17	18	14	18	18	18
Weighted average	5	3	40	15	12	nd	nd	26	12	2	3	3	7	2	16	302	37
Max value	7	4	60	26	26			85	18	4	6	5	10	3	24	362	53
Min value	2	1	24	13	4			2	6	2	2	2	5	1	8	230	26
Weighted *s*	1	0.93	11	5	9			22	4	0.5	1	0.9	2	0.4	4	37	8
CCLR-BE																	
N	38	38	38	38	22	17	16	38	38	38	38	36	37	35	38	38	38
Weighted average	6	2	43	12	8	10	7	19	14	3	6	4	12	4	24	531	113
Max value	45	5	128	23	22	37	20	71	36	5	10	6	19	5	34	673	187

Table 3 (*continued*)

Data	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	Ca^{2+}	H^+	CE	V	Pb	Cr	Cu	Ni	Mn	Al	Fe
CCLR-BE																	
Min value	0.6	0.8	21	4	3	2	2	1	4	2	2	2	7	2	12	324	85
Weighted *s*	8	1	20	5	11	14	5	18	7	0.7	2	0.7	3	0.8	6	72	19
ZI-BE																	
N	39	39	39	39	15	17	24	39	39	39	38	38	39	36	39	39	39
Weighted average	6	2	42	10	8	4	7	25	16	4	5	3	16	2	19	413	88
Max value	19	6	115	36	22	7	14	138	40	6	7	5	27	3	34	607	113
Min value	2	0.6	16	4	3	2	5	1	5	2	3	2	12	1	10	281	74
Weighted *s*	4	1	25	8	8	1	3	26	8	1	1	0.8	4	0.6	6	83	9

and quantified by interpolation on the calibration curves of five standard 10–50 μg/l solutions for V, Cu, Cr, Ni, Pb, Fe and Al and 5–30 μg/l standard solutions for Mn, from Perkin Elmer certified commercial 1000 mg/l solutions traceable to NIST.

Detection limits in μg/l, determined by the IUPAC method, were 0.8 for V, 1.5 for Cu, 1.1 for Pb, 1.5 for Cr, 1.0 for Mn, 0.8 for Ni, 4.5 for Fe and 5.6 for Al. Blanks were analyzed for both metals and inorganic ions to make the corresponding corrections.

3. Results and discussion

3.1. Chemical composition

Table 3 presents volume-weighted average, maximum and minimum values obtained for conductivity, inorganic ions and heavy metals in precipitation samples collected at the 11 sampling sites. The most acidic weighted average pH values were found at REC-HER (4.58), ICE-SJ (4.55) and MSP-SJ (4.43), sites located in commercial areas with high traffic density. For these three sites, between 6 and 9.5% of the events showed a pH higher than 5.60, which is the pH of cloud water in equilibrium with atmospheric carbon dioxide (Charlson and Rodhe, 1982). Sampling sites located in areas with lower rates of vehicular traffic are BN-SJ (4.82), ILA-HE (4.85) and MEC-HE (4.82), which showed less acidic weighted average pH, with 25–26% of the events having values greater than 5.60. Concentrations of the major ionic species present in precipitation samples were in the following order: $SO_4^{2-} > NH_4^+ > Ca^{2+} > Na^+$, with ion percentages 41.4, 12.0, 10.9 and 9.1 respectively. Al, Fe and Mn were the most abundant trace metals. Table 4 shows the relation between the total accumulated precipitation data measured by the National Meteorological Institute in each site and the precipitation collected during this sampling period.

Table 4
Total volume of precipitation collected at different sampling sites located in the metropolitan area of Costa Rica, August–November 2007.

Sampling point	Total volume of precipitation collected/mm	Accumulated precipitation/mm 2007
BN-SJ	521.4	2258.6
MSP-SJ	676.6	2258.6
SPM-SJ	715.7	2348.1
MSJ-SJ	532.5	2348.1
ICE-SJ	432.6	2407.6
REC-HE	751.9	3074.3
ILA-HE	716.9	3074.3
MEC-HE	733.7	3074.3
CBN-HE	262.2	2407.6
ZI-BE	642.3	2756.5
CCLR-BE	573.8	2756.5

The influence of the origin of the air masses over the chemical composition of the bulk precipitation has been described by several studies (Davies et al., 1990; Ezcurra et al., 1988; Norman et al., 2001; Samara et al., 1992).To analyze the effect of wind speed and wind direction over the content of ions and metals in the collected samples, the wind trajectories were classified into 4 groups. The first group was from 0° to 90°, the second group from 90° to 180°, the third group from 180° to 270° and the fourth group from 270° to 360°. As a result, Fig. 3 shows the average concentrations of metals (μg/l) and ions (μequv/l) according to the quadrant trajectory for some of the sampling points. For the sampling points, the predominant wind directions are southwest for approximately 60–50% of the occasions and southeast for the rest. The concentrations of the chemical species in the bulk precipitation samples resulted higher when the air masses moved southeast, probably due to the presence of higher industrial activity nearby, compared to the residential areas located southwest. Additionally, it is important to remark that the concentrations of the ionic species resulted higher at wind speeds lower than 1.5 m/s. This can be explained by the fact that when the wind speed decreases the remotion of particles and gases are lower, this allows a higher wash out during the rain events.

3.2. Marine contribution

To estimate not only the marine contribution to the chemical composition of total precipitation but also contributions from other sources, several ratios were calculated as sea salt fractions and enrichment factors. To calculate these ratios, Na was taken as the point of reference assuming that it has a predominantly marine origin (Kulshrestha et al., 1996). Table 5 shows Cl^-, SO_4^{2-}, K^+ and Ca^{2+} ratios with respect to Na^+. Only the ratios involving SO_4^{2-}, K^+ and Ca^{2+} were higher than the ratios recorded for sea water. These values, higher than expected, can be attributed to contributions from anthropogenic and crustal sources. Higher values of these ratios with respect to Na^+ suggest origins other than marine. The fractions of sea salt and non-sea salt were calculated. Only Cl^- did not show sources not related to marine aerosols. Enrichment factors of different species with respect to Na were estimated using the following equation

$$\mathrm{EFc} = \frac{X / \mathrm{Na}^+ \text{ bulk precipitation}}{X / \mathrm{Na} \text{ sea water}} \quad (1)$$

where X is the ion of interest.

3.3. Enrichment factors

Enrichment factors enable estimation of the degree of enrichment for a given metal with respect to its relative abundance in crustal material. Enrichment factors can be estimated according to the following equation (Duce et al., 1975):

$$\mathrm{EF} = \frac{(X / \mathrm{Al})\ \text{bulk precipitation}}{(X / \mathrm{Al})\ \text{crustal}} \quad (2)$$

where X represents the element of interest. If the value of the enrichment factor is close to unity, the item has a predominantly crustal origin. However, due to differences between crustal compositions in different regions of the world, enrichment factor values between 1 and 10 are considered to indicate natural origin.

Table 5
Comparison of sea water ratio with components of bulk precipitation.

	Cl^-/Na^+	SO_4^{2-}/Na^+	K^+/Na^+	Ca^{2+}/Na^+
Ratios in sea water	1.16	0.125	0.227	0.0218
Ratios in total precipitation	0.6	4.07	0.53	1.07
Fraction from sea salt	100	0.031	0.425	0.02
Fraction from sources other than sea salt		0.969	0.575	0.98
Enrichment factor	0.52	33.9	2.3	49.10

In this study, Al was used as a reference to estimate these factors. Upper continental crustal concentration was taken from Taylor and McLennan (1985).

V, Cr, Ni, Mn and Fe show enrichment factor values of less than 10, as can be seen in Table 6, which suggests that they are

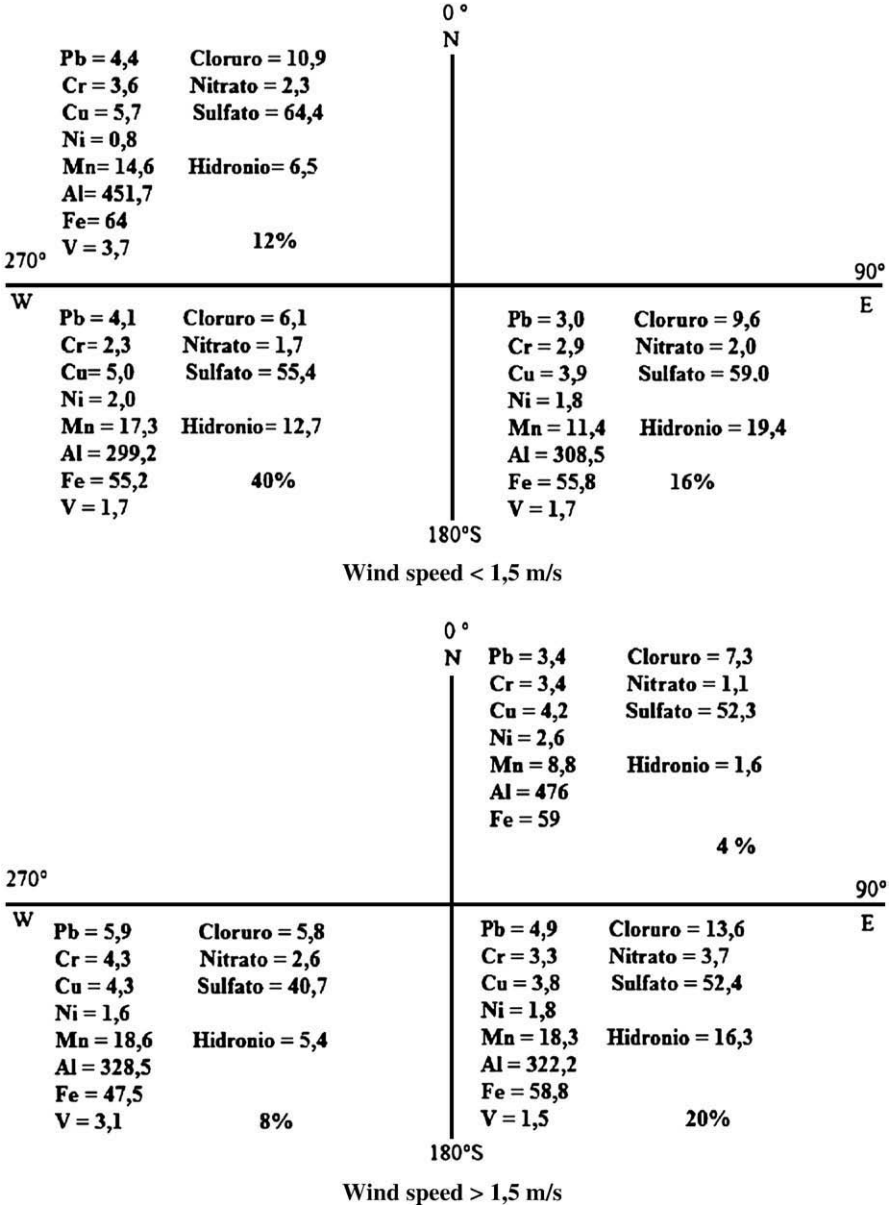

Fig. 3. Relation between wind trajectories and chemical composition of bulk precipitation samples collected in the monitoring sites.

Table 6
Enrichment factors for metal species present in bulk precipitation samples collected in the metropolitan area of Costa Rica, August–November 2007.

Sampling site	V	Pb	Cr	Cu	Ni	Mn	Fe
BN-SJ	7.28	73.20	4.02	22.02	8.44	3.65	0.27
MSJ-SJ	2.87	47.39	1.71	24.57	3.62	3.76	0.32
SPM-SJ	5.75	60.67	4.04	26.40	5.06	5.03	0.26
ICE-SJ	3.23	26.09	2.67	18.19	3.11	1.46	0.22
MSP-SJ	4.11	51.86	3.01	23.98	7.21	5.04	0.27
REC-HE	1.87	36.13	2.15	29.07	4.21	3.92	0.31
ILA-HE	2.52	39.34	2.34	17.74	1.95	3.85	0.27
MER-HE	4.21	25.98	2.80	14.61	4.87	1.44	0.19
CBN-HE	6.12	52.03	3.90	43.06	6.39	4.33	0.20
CCLR-BE	4.73	59.20	2.76	42.19	7.27	3.61	0.34
ZI-BE	7.33	66.88	3.05	70.38	5.16	3.66	0.35

mostly due to dust of crustal origin. Only Pb and Cu showed factors that suggest moderate enrichment compared to average crustal composition, indicating a contribution from anthropogenic sources.

3.4. Neutralization factors

Precipitation acidity is mainly controlled by strong acids such as H_2SO_4 and HNO_3. Taking into account that SO_4^{2-} and NO_3^- ions are the principal components of precipitation acidity, fractional acidity (FA) can be calculated as (Balasubramanian et al., 2001):

$$FA = \frac{[H^+]}{([\text{nss}\, SO_4^{-2}] + [NO_3^-])}. \quad (3)$$

If this ratio is one, acidity generated by strong acids is not completely neutralized. Fig. 4 shows the differences in fractional acidity of precipitation samples by sampling site. It is important to note that for sites in the city of Heredia, the fractional acidity obtained is less than that recorded at the other sites, only approximately 70–76% of the acid being neutralized by alkaline constituents, a rate much higher than that recorded in San Jose and Belen. The relative contribution of NO_3^- to acidification can be determined through the ratio $[NO_3^-]/([NO_3^-]+[\text{nam}\ SO_4^{-2}])$, resulting in a value between 0.045 and 0.055, showing that approximately 4.5–5.5% of the total acidity of precipitation is due to NO_3^-, while 95–96.5% of acidity can be attributed to SO_4^{2-}.

Table 7
Variation of fractional acidity, original acidity and relation between potential neutralization with regard to potential acidity of bulk precipitation collected at the sampling sites located in the metropolitan area of Costa Rica, 2007.

Sampling site	Fraccional acidity	Original acidity (μeq/l)	PN/PA
BN-SJ	0.212	62.6	0.86
MSJ-SJ	0.356	66.5	0.78
SPM-SJ	0.474	92.7	1.35
ICE-SJ	0.496	85.2	1.08
MSP-SJ	0.492	80.0	0.97
REC-HER	0.303	95.1	1.01
ILA-HER	0.303	71.4	1.07
MER-HER	0.307	37.1	1.31
CBN-HER	0.567	39.5	0.82
CCLR-BEL	0.384	57.7	0.82
EINT-BEL	0.478	67.8	0.85

According to Galloway et al. (1987), the hydrogen ion concentration measured reflects precipitation acidity after neutralization from air bases, especially NH_4^+ and Ca^{2+}. However the original acidity can be estimated from the sum $[H^+]+[NH_4^+]+[Ca^{+2}]$ in order to make a comparison between estimated and measured acidity.

Table 7 shows the spatial variation of the ratio between measured and original acidity, calculated for total precipitation collected in the metropolitan area of Costa Rica. Momin (1990) reported that original acidity is about two orders of magnitude greater than measured acidity. The author suggests that the neutralization reaction is faster and more extensive during early stages of precipitation events, when dust particles are more abundant. In contrast, the pH of precipitation is low during the last stages when the pH is higher and particle quantity is reduced.

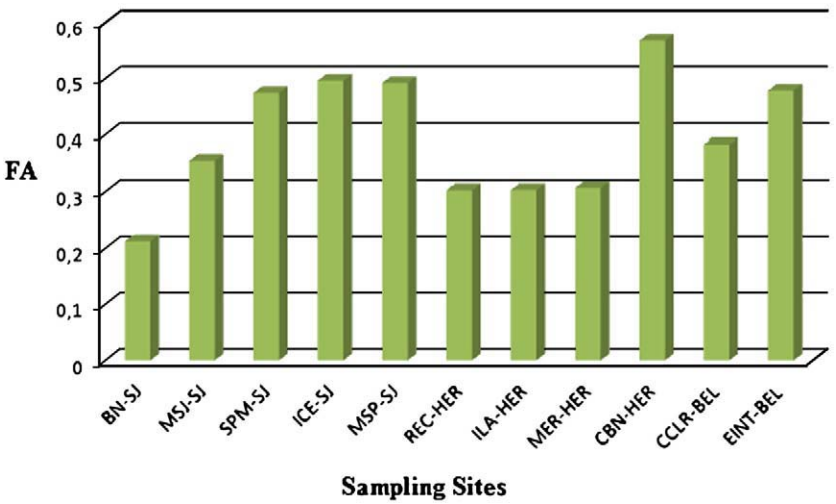

Fig. 4. Variation of fractional acidity in bulk precipitation samples collected in sampling sites of the Metropolitan Area of Costa Rica, 2007.

Table 8
Comparison of SO_4^{2-}/NO_3^- ratio values obtained for the metropolitan area of Costa Rica with other cities.

Sites	SO_4^{2-}/NO_3^-	Reference
Guaiba, Brazil	8.70	Migliavacca et al. (2005)
Figueira	5.30	Flues et al. (2002)
Singapore	3.50	Balasubramanian et al. (2001)
Spain	2.22	Avila and Alarcon (1999)
Italy	3.10	Le Bolloch and Guerzoni (1995)
Costa Rica	18.6	Current study

The role of NH_4^+ and Ca^{+2} was validated by calculating neutralization factors according to the equations proposed by Parashar et al. (1996):

$$FN\,NH_4^+ = \frac{[NH_4^+]}{([SO_4^{-2}] + [NO_3^-])} \quad (5)$$

$$FN\,Ca^{+2} = \frac{[Ca^{2+}]}{([SO_4^{-2}] + [NO_3^-])}. \quad (6)$$

Average neutralization factor values for all sampling sites were found to be 0.53 and 0.33 for Ca^{+2} and NH_4^+ respectively. This indicates that both species play an important role in neutralization processes in samples of total precipitation. In order to analyze the balance between acidity and alkalinity, the ratio between the neutralization potential and the potential for acidification was estimated; $PN/PA = ([nss\ Ca^{+2}] + [NH_4^+])/([nss\ SO_4^{-2}] + [NO_3^-])$. Table 5 shows the values for this ratio. The average value of PN/PA, 0.92, indicates that there is a predominance of acid rather than alkaline species in samples of total precipitation, except for sites located in the city of Heredia.

3.5. SO_4^{2-}/NO_3^- ratio

The SO_4^{2-}/NO_3^- ratio can be used to indicate the contribution of anthropogenic sources to atmospheric precipitation in urban areas (Migliavacca et al., 2004). The results obtained in this study are shown in Table 8, and are compared with those reported in other cities; Guaiba, Figueira, Singapore, and cities in Spain and Italy. As can be seen in Table 6, SO_4^{2-}/NO_3^- the value of the ratio recorded in the metropolitan area of Costa Rica proves to be higher than values reported for other urban centers. This is because of significant sulfur dioxide emissions resulting from two main causes; first, the increase in gas emissions from the Turrialba volcano during 2007. The volcano's plume, due to the prevailing wind direction, is blown directly to this region of Costa Rica. The second cause is the high sulfur content (3500–4000 ppm) of diesel used in Costa Rica. The value recorded for this ratio in 2007 was higher than the 9.2 reported by Herrera and Rodríguez (2007) for 2006.

Table 10
Precipitation flux for ionic and metal species (kg/km^2) present in samples collected in monitoring sites, during August–November 2007.

Sampling sites	Cl^-	NO_3^-	SO_4^{2-}	Na^+	V	Pb	Cr	Cu	Ni	Mn
BN-SJ	169	83	1364	181	1.2	2.2	1.6	2.2	1.0	8.3
MSJ-SJ	244	123	1280	183	0.7	1.4	0.7	2.2	0.6	7.6
SPM-SJ	153	123	1639	219	1.4	2.7	2.1	3.5	1.2	15.0
ICE-SJ	77	70	1806	225	0.1	0.5	0.7	1.0	0.3	1.8
MSP-SJ	198	182	1579	157	1.2	2.1	1.7	2.9	1.5	13.6
REC-HER	139	121	1919	264	0.8	2.2	1.8	5.3	1.4	15.8
ILA-HER	769	161	1712	277	1.2	2.5	2.0	3.4	0.7	16.6
MER-HER	165	131	1575	254	0.8	0.8	1.6	2.1	0.6	4.4
CBN-HER	44	43	1457	176	0.6	0.8	0.7	1.9	0.3	4.2
CCLR-BEL	114	81	1070	191	1.9	3.3	2.1	6.2	2.0	13.5
EINT-BEL	128	82	1175	225	2.6	3.3	2.0	10.3	1.4	12.0

3.6. Statistical analysis

Table 9 shows the Spearman correlation coefficient matrix of the trace metals and ion species present in total precipitation. Three ion species (K^+, Cl^- and Na^+) show significant correlation coefficients due to their predominantly marine origins. The relationship between H^+ and Cl^- ions is not significant, indicating that a small part of free acidity can reasonably be attributed to Cl^-.

Correlations between acid ionic species (H^+, SO_4^{2-}, NO_3^-) suggest partial neutralization of acidity. Correlation between SO_4^{2-} and NO_3^- was expected because of the emission of the precursor SO_2 and NO_x and the similarity of their behavior in total precipitation. NH_4^+ and SO_4^{2-} showed a stronger correlation between this cation and NO_3^-. This is consistent with

Table 9
Spearman correlation coefficient for inorganic ions and metals present in samples of bulk precipitation, collected in La Ribera Commercial Center, Belén Costa Rica, August–November 2007.

	Cl^-	NO_3^-	SO_4^{2-}	Na^+	NH_4^+	K^+	H^+	V	Pb	Cr	Cu	Ni	Mn	Al	Fe
Cl^-	1.000														
NO_3^-	0.071	1.000													
SO_4^{2-}	0.160	**0.654**	1.000												
Na^+	**0.821**	0.115	0.423	1.000											
NH_4^+	0.318	**0.573**	**0.707**	0.425	1.000										
K^+	**0.587**	−0.057	−0.109	**0.689**	0.293	1,000									
H^+	0.112	**0.521**	**0.589**	−0.004	0.156	−0.239	1.000								
V	0.019	−0.034	**0.483**	0.352	**0.593**	−0.204	0.288	1,000							
Pb	−0.140	−0.068	**0.540**	0.204	−0.126	0.269	−0.315	**0.583**	1.000						
Cr	0.315	0.101	−0.100	0.116	0.120	0.025	−0.033	0.104	0.044	1.000					
Cu	0.015	0.106	**0.485**	−0.257	−0.147	−0.097	0.132	0.029	**0.493**	−0.217	1.000				
Ni	−0.143	0.111	0.152	0.089	0.080	0.207	−0.096	0.150	**0.611**	0.173	**0.478**	1,000			
Mn	−0.072	**0.472**	0.249	−0.230	**0.539**	0.296	0.210	**0.570**	**0.504**	−0.035	0.072	**0.507**	1,000		
Al	−0.037	0.147	0.118	0.108	0.221	0.358	0.121	0.206	0.201	−0.006	0.102	**0.556**	**0.595**	1,000	
Fe	−0.251	0.057	−0.146	−0.409	−0.190	−0.102	0.293	0.038	−0.116	0.128	0.197	0.058	0.146	0.076	1,000

Values in bold are significant at $p<0.05$, $N=38$.

Table 11
Daily precipitation flux (meq/m^2 d) for ions in diverse sampling sites.

	Urban areas			Rural and remote areas		
	San José, Costa Rica	Northeast of the United States [a]	Sao Paulo, Brasil [b]	Northeast of Spain [c]	Northwest of Europe [d]	Candiota Brasil [e]
Na^+	0.057	0.055	0.010	0.045		0.235
Cl^-	0.069	0.068	0.020	0.058		0.290
SO_4^{2-}	0.463	0.178	0.055	0.184	0.041	0.227
NO_3^-	0.027	0.082	0.050	0.044	0.014	0.178

[a] Munger and Eisenrich (1983).
[b] Lara et al. (2001).
[c] Alstuey et al. (1999).
[d] Galloway et al. (1982a,b).
[e] Migliavacca et al. (2004).

observations on the $NH_4^+/SO_4^{2-}/NO_3^-$ system, where the free NH_3 reacts first with H_2SO_4 to form $(NH_4)_2SO_4$ and $(NH_4)HSO_4$, and remaining NH_3 can then form NH_4NO_3 by chemical interaction with HNO_3 (Seinfeld and Pandis, 1998).

The results presented in Table 9 show that predominant combinations between chemical species present in the total deposition samples are NaCl, KCl, H_2SO_4, $(NH_4)_2SO_4$, HNO_3, NH_4NO_3 and $CaSO_4$. These can be formed in water droplets through contact with atmospheric aerosols and the subsequent reaction of gaseous species (Miller and DePena, 1972). There are no significant differences between correlation patterns found for total precipitation sampling sites. Positive and negative correlations can be observed between the metals Al–Mn, Ni–Mn, Ni–Al, Cu–Ni, Pb–Cu, Pb–Ni and Pb–Mn. It is important to note that the correlations of some metal species such as V, Pb, Cu and Mn with SO_4^{2-} and NO_3^- may indicate their possible anthropogenic origin, according to several authors (Kim et al., 2000; Kaya and Tuncel, 1997).

3.7. Determination of precipitation flows for ionic species and heavy metals

Precipitation flows for each of the chemical species present in the samples can be calculated using the following equation (Liancong et al., 2007):

$$FD = \Sigma C_i \times RR_i \times 10^{-3} \quad (7)$$

where RR_i is the level of pluvial precipitation (mm) for day i, C_i is the concentration of chemical species of interest present in the sample of total precipitation (mg/L) collected during day i and FD is the deposition flow (kg/km^2) for the sampling period from August to November 2007. Table 10 shows precipitation flow for total samples collected during the sampling period. As can be seen, in the case of Na, a southeast to northwest gradient can be observed, the highest rates being recorded at sites located in the central canton of Heredia, where the chemical compositions of samples of PM_{10} particles and precipitation are more influenced by marine aerosols. In addition, it can be noted that flows of ion species that can act as nutrients in aquatic ecosystems, such as NO_3^- and SO_4^{2-}, have high values, producing a direct impact on the chemistry of precipitation over aquatic ecosystems. The reason is that they stimulate primary production in these environments, as reported by various authors (Gao, 2002; Xu and Qin, 2005; De Leeuw et al., 2003). In fact, these authors have determined that an average precipitation of 0.8 mmol of N/m^2 d can stimulate production at a rate of nearly 5.3 mmol C/m^2 d in the North Sea.

In Table 11 the deposition flow values obtained for the city of San José can be compared with the values for other regions. It can be concluded that SO_4^{2-} and Na^+ values are higher, probably due to the influence of SO_2 volcanic emissions and high gasoline sulfur content. For the case of SO_4^{2-} and Na^+, this could be attributed to the influence of sea spray carried by air currents from the Caribbean Sea and Pacific Ocean in a relatively narrow country.

4. Conclusions

The most abundant ions and trace metals found in the total precipitation samples collected in the Costa Rica metropolitan area are Na^+, SO_4^{2-} and Al, Fe. The chemical composition of precipitation indicated the contribution of marine aerosols, especially in the case of Na, K and Cl.

Sampling sites located in high traffic flow areas had the most acidic pH values. Only 5% of the total samples had pH values below 5.60. 5.5% of total precipitation acidity is due to NO_3^-, while 95–96.5% can be attributed to SO_4^{-2}. Both ions are provided mostly by anthropogenic sources, and the ratio between them (SO_4^{-2}/NO_3^-) shows values higher than those recorded for other urban centers. Most of the metals measured in total precipitation have a crustal origin, with the exception of Pb and Cu, which are enriched by contributions from anthropogenic sources. In future studies, it will be important to analyse the difference in chemical composition, between wet and bulk precipitation.

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