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Relations Between Bulk Precipitation, PM_{10} Composition and Meteorological Conditions in the Metropolitan Area of Costa Rica

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Abstract: Concentrations of inorganic ions (Cl^-, H^+, SO_4^{2-}, NO_3^-, NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+}) and metals (V, Ni, Cu, Pb, Cr Mn, Al, Fe) in bulk precipitation and PM_{10} samples collected in the metropolitan area of Costa Rica were analyzed. Good correlations between acidity in bulk precipitation with the concentrations of aerosols in the air were observed. The scavenging of the pollutants from the air directly affects the pH and composition of the bulk precipitation. The major ions in bulk precipitation in the metropolitan area of Costa Rica were SO_4^{2-}, NH_4^+, Ca^{2+}, Na^+ ion percentages with 41.4, 12.0, 10.9 and 9.1 respectively. Al, Fe and Mn were the most abundant trace metals. The alkaline cations, NH_4^+ and Ca^{2+}, acted as acid neutralizers and buffered the acidity of bulk precipitation. Meteorological conditions presented during the events determine the composition of bulk precipitation samples.

Keywords: Water soluble ions, PM_{10}, trace metals, bulk precipitation, Costa Rica.

1. INTRODUCTION

The urban atmosphere is subjected to large inputs of anthropogenic contaminants coming from both stationary (industries) and mobile sources (road traffic) [1, 2, 3]. According to their physical and chemical properties, these pollutants are partitioned between particulate, liquid, and vapor phases and are subsequently transported to the Earth's surface through dry and wet deposition. During dry periods, particles are removed efficiently only by dry processes such as impaction and diffusion to surfaces of objects while, in wet periods, particles and gases are removed mainly by precipitation [4]. For particulate pollutants, removal fates are strongly related to particle size. Large particles are efficiently removed by gravitational settling. For small particles, especially those with diameters below 0.1 µm, Brownian diffusion becomes increasingly important with decreasing particle size. Brownian motion is especially important in sublayers (i.e., just above the air/sea interface) where turbulence is weak. Inertial impaction is an important removal mechanism when the momentum of a particle is sufficient to maintain a nearly linear trajectory in a moving air mass. Inertial impaction is important for particles with aerodynamic diameters between 0.5 and 15 µm but is highly dependent on particle size and wind velocity [5].

In principle, "bulk precipitation" is defined as the sum of wet-only deposition and of sedimenting (dry) particles to a sample collector in ambient air. In practice, however, this sum can be affected by simultaneous deposition of gases and fine aerosols to the sample collector. Consequently, "bulk precipitation" is often defined operationally as the total deposition of material to a continuously-open sample collector [6].

According to several authors [7,8], bulk precipitation composition results from two series of mechanisms operating consecutively. The first processes, grouped together under the term 'rainout', correspond (i) to condensation of water vapour on aerosol particles during the cloud droplets formation, (ii) to subsequent attachment of aerosol particles to the cloud elements and (iii) to incorporation of gases surrounding the droplets by aqueous-phase reactions. The second set of processes refers to the 'washout' of the below-cloud atmosphere during precipitation events by raindrops, which carry and dissolve particles and gases along their fall. Therefore, chemical composition of bulk precipitation will be influenced by both, the composition of aerosols and gases at the level of cloud formation, and by the nature of gases and particles in suspension in the air masses below the cloud level during rainfall [9].

Wind force and direction, before and during precipitation, are thus important parameters to take into account to explain bulk precipitation chemistry as a function of the localization and the importance of natural (marine, crustal, biological, volcanic) and anthropogenic (industrial, traffic, heating, agriculture) sources of ions and metals in the surroundings of the sampling location. Moreover, rainfall volume is a key parameter for rain composition as it determines the degree of washout of the atmosphere, influencing therefore the global concentration of rain. Relationships between ion concentration and rainfall rate

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*Address correspondence to this author at the Laboratorio de Análisis Ambiental, Escuela de Ciencias Ambientales, Universidad Nacional. Campus Omar Dengo, Heredia, Costa Rica; Tel: (506) 22773292; Fax: (506) 22773696; E-mail: jherrer@una.ac.cr have also been reported [10]. Finally, the duration of the rain-free period, preceeding a rain event, influence the concentration of suspended particles and gases at rain beginning.

This paper aims to provide a characterization of some factors that determine the bulk precipitation chemical composition in the metropolitan area of Costa Rica. This region of Costa Rica contains 75% of the country's vehicle fleet (approximately 734 200 units), 75% of the industry, and 60% of the population (2 580 000), according to data from the most recent census [11]. The lack of urban planning and population growth has been affecting air quality during the last 20 years in this region of the country.

2. MATERIALS AND METHODS:

2.1. Site Selection and Sampling Procedures

2.1.1. PM_{10}

For the PM_{10} sampling, five monitoring sites were selected (Table **1**). The sites were representative of commercial, industrial and residential areas, all located in the metropolitan area of Costa Rica. Sampling campaign was conducted between May and November 2007. Samples were collected three times a week. To collect the samples, five high volume air samplers, Thermo Andersen with MFC (Mass Flow Controller) were used during 24 ± 1 h, with a flow rate of 1.13 ± 10% m^3min^{-1}. Flow calibration of each sampler was performed with a calibrated critical orifice, TISCH VARIFLO model 454. For sampling collection, Whatman CAT No. 1829-932 fiberglass filters were used twice a week. Whatman CAT No. 1851-865 quartz filters were used for the subsequent analysis of metals at least once a week. Those filters were conditioned at least 24 h in a desiccator under the following conditions: temperature of 15-30 °C and humidity less than 40%, before being weighted in an analytical balance.

2.1.2. Bulk Precipitation

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. At each sampling site, two devices were placed to capture bulk 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% HNO_3 and then rinsed several times with DW. Sample collection during the campaign took place in periods 1 to 2 days long (depending on precipitation frequency), during the months of August to December, 2007. Collected volumes ranged from 20 to 95 ml.

In the Metropolitan Area of Costa Rica, the climate is characterized by show a dry season between December and April, with wind speeds close to 30 kmh^{-1} and a rainy season, May-November, where the trade winds decrease its intensity, bringing the breeze of the Pacific, heading from Southwest, enters to this area and forms a "front breeze", encouraging the formation of cumulus-kind clouds of vertical development enough to cause rains and thunderstorms. Table **2** 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.

2.2. Chemical Analysis

2.2.1. Inorganic Ions

For PM_{10} samples from each filter, a strip of 2.54 cm wide and 23.0 cm in length was cut. Then, it was placed in a 150 ml Beaker, 75 ml of deionized water (DW) was added. After that, they were located in an ultrasonic bath tempered

Table 1. Description of Sampling Sites for the Collection of PM_{10} in the Metropolitan Area of Costa Rica

	Sampling Site Identification	Province	District	Site Description
1	CAT-SJ	San Jose	Facilities of the Metropolitan Cathedral Metropolitana in the City of San Jose	-Commercial area with high traffic flow -6,75 m of the street and 3 m above the ground
2	JE-SJ	San Jose	Building of the Board of Education in San Jose	-Transition between comercial and residencial zone. Low traffic flow - 8 m of the highway and 2,5 m above the ground level
3	REC-HE	Heredia	Balcony of the Rectory Building of the National University	-Commercial zone with high traffic flow -5,5 m of the highway and 6 m above the ground level
4	GOB-HE	Heredia	Building of the Governorship of Heredia	-Transition between comercial and residencial -7 m of the highway and 5,5 m above the ground level
5	CCLR-BE	Heredia	Flat roof of La Ribera Commercial Center	-Industrial zone, Metropolitan Area wind exit -6 m of the highway and 5 m above the ground

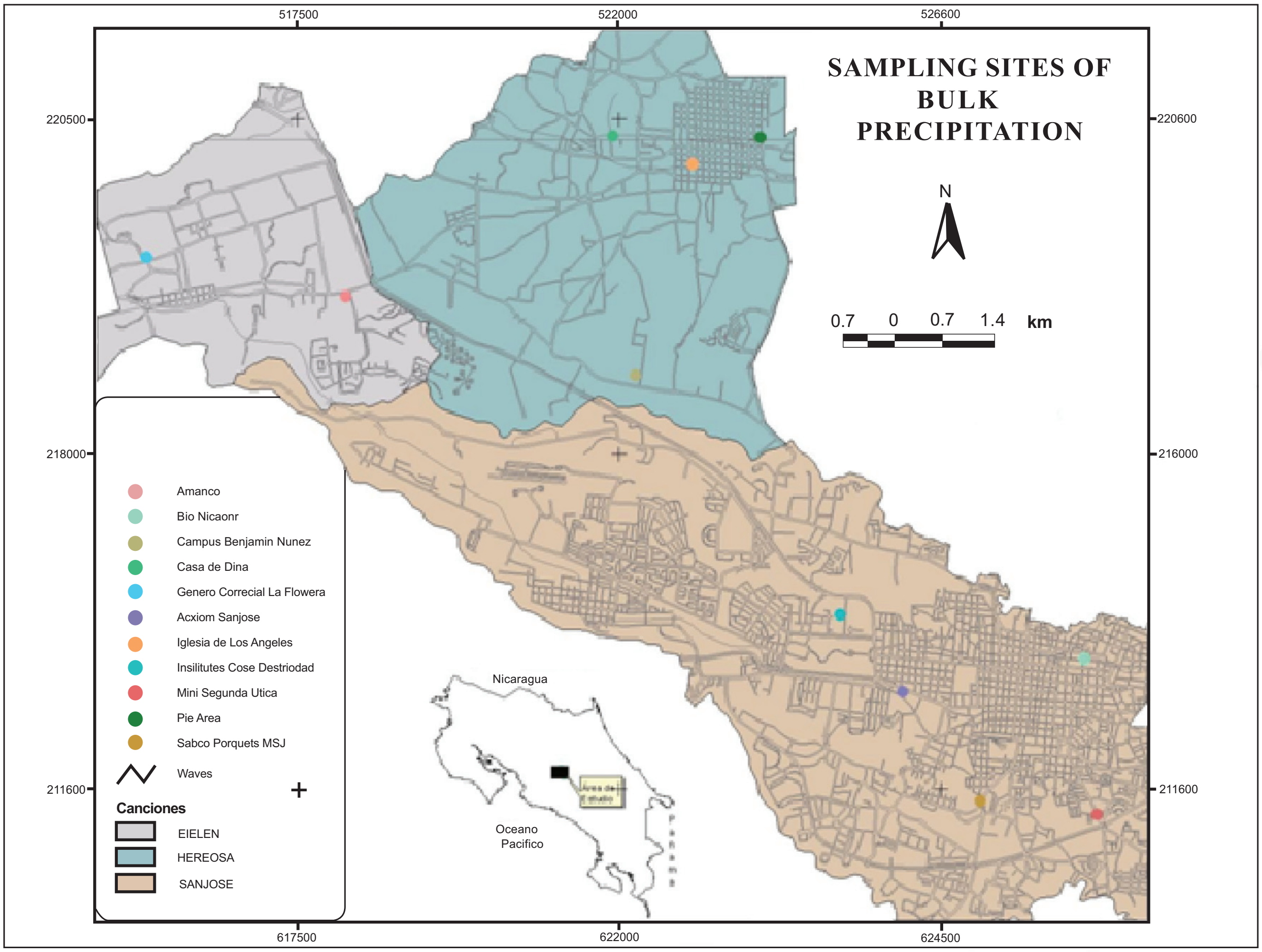


Fig. (1). Sampling sites for bulk precipitation in the Metropolitan area of Costa Rica.

at 35°C for 60 minutes. The obtained extract was transferred quantitatively to a 100 ml ball flask. And, from this flask, a portion to be analyzed was filtered.

In the case of bulk precipitation, once the samples had been collected, they were transported to the laboratory. Sample volumes were measured with a graduated cylinder. Conductivity and pH were then measured using OAKTON equipment, model pH/CON 510. These measurements were made a maximum of three hours 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) ºC, and ion quantification was performed within 48 hours.

Analysis of ionic species in PM$_{10}$ and bulk precipitation, was performed by microbore ion exchange chromatography with suppression using a DIONEX ICS-3000 equipment with a quaternary pump, according to the specifications listed in Table **3**. Ionic species were identified and quantified by interpolation on a calibration curve of seven standard solutions of 0.25 to 10 mgl^{-1} for anions and 0.10 to 8 mgl^{-1} for cations.

Table 2. Total Volume of Precipitation Collected at Different Sampling Sites Located in the Metropolitan Area of Costa Rica, August–November 2007

Sampling Site	Total Volume of Precipitation Collected/mm	Accumulated Precipitation in 2007/mm
BN-SJ	521,4	2259
MSP-SJ	676,6	2259
SPM-SJ	715,7	2348
MSJ-SJ	532,5	2348
ICE-SJ	432,6	2408
REC-HE	751,9	3074
ILA-HE	716,9	3074
MEC-HE	733,7	3074
CBN-HE	262,6	2408
ZI-BE	642,3	2756
CCLR-BE	573,8	2756

Table 3. Instrumental Conditions Used to Determine Ionic Species Present in Collected Samples of Bulk Precipitation and PM_{10}

	Anions	Cation
Detector	Electrical conductivity attached to suppresor	Electrical conductivity attached to suppresor
Column	Dionex IonPac AS9-HC Particle size: 9 µm (2 x 250 mm)	Dionex IonPac CS12A Particle size: 9 µm (2 x 250 mm)
Electrolytic suppresor	Dionex ASRS ULTRA II	Dionex CSRS ULTRA II
Mobile phase	Na_2CO_3 dissolution 9 $mmol^{-1}$ to pH = 10.88	Dissolution of methasulphonic acid 20 $mmol^{-1}$
Injection volume	10 µl	10 µl
Mobile phase flow	0.25 $mlmin^{-1}$	0.25 $mlmin^{-1}$
Column temperature	30°C	30°C

In addition, detection limits of ions were determined by taking 10 samples from different points of a blank filter 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. The results are shown in Table **4**.

2.2.2. Metals

For PM_{10} samples from each quartz filters, a strip of 2.54 cm wide and 23.0 cm length was cut. It was placed in a 150 ml beaker and then, 25 ml of DW water and 5 ml of concentrated nitric acid were added. The samples were taken to be almost dry in a warming plate. The remainder was quantitatively transferred to a 25 ml flask. The extraction process was repeated once more.

In the case of bulk precipitation samples, an aliquot of 25 ml 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 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 and quantified by interpolation on the calibration curves of five standard 10 to 50 $\mu g\ l^{-1}$ solutions for V, Cu, Cr, Ni, Pb, Fe and Al and 5 to 30 $\mu g\ l^{-1}$ standard solutions for Mn, from Perkin Elmer certified commercial 1000 $mg\ l^{-1}$ solutions traceable to NIST. The detection limits are shown in Table **4**.

2.2.3. Quality Control

Blanks of all glassware and plastic-ware used were analyzed. Concentrations on blanks were below the detection limits. For metals and inorganic ions, field blank samples were analyzed, obtaining concentrations of less than 2% of those found in samples. The results obtained for the field blank samples were used to make the proper corrections during sample analysis. Precision and bias of analysis were determined from quality control check samples prepared in the laboratory. For this study 7 equal strips of a single filter and 7 portions of one bulk precipitation sample were spiked

Table 4. Detection Limits Obtained for the Analysis of Ion and Metal Concentration in PM_{10} Particles (μgm^{-3} for Ions and ngm^{-3} for Metals) and Bulk Precipitation Samples (mgl^{-1} for Ions and μgl^{-1} for Metals)

Type of Matrix	SO_4^{2-}	NO_3^-	Cl^-	PO_4^{3-}	F^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	V	Pb	Cr	Cu	Ni	Mn	Al	Fe
Glass fiber filter	0.08	0.04	0.11	0.26	0.02	0.87	0.13	0.06	0.05	0.02								
Quartz filter	0.03	0.01	0.05	0.06	0.01	0.10	0.05	0.02	0.01	0.01	0.1	0.4	0.9	0.8	0.5	0.4	0.9	0.5
Bulk precipitation	0.09	0.03	0.08	0.08	0.03	0.05	0.03	0.05	0.07	0.03	0.8	1.3	2.0	2.3	1.1	2.4	2.8	3.5

Table 5. Bias and Standard Deviation Percentages Obtained for the Analysis of Ions and Metals in PM_{10} and Bulk Precipitation Samples

PM 10 Collected in Quartz Filter																		
	SO_4^{2-}	NO_3^-	Cl^-	PO_4^{3-}	F^-	Na^+	K^+	Ca^{2+}	Mg^{2+}	NH_4^+	V	Pb	Cr	Cu	Ni	Mn	Al	Fe
% Bias	0.25	-0.51	0.63	0.65	0.85	1.3	-1.1	2.4	1.7	3.2	1.6	0.2	2.5	-0.8	-3.8	-4.7	3.2	4.0
% Standard deviation	3.2	3.7	2.8	1.1	1.6	0.8	1.4	2.5	2.1	3.5	4.7	5.3	4.4	4.3	3.6	7.2	6.1	5.7
Bulk Precipitation																		
% Bias	0.75	1.2	1.7	0.8	-2.1	0.9	-1.3	2.1	1.5	-0.9	0.9	1.2	2.1	1.5	-1.2	3.2	2.8	3.3
% Standard deviation	2.7	1.6	1.9	2.0	1.7	0.9	0.7	1.3	1.1	2.2	3.6	2.6	3.2	3.7	2.5	4.4	3.9	5.1

Table 6. Volumen Weighted Averages for the Concentration of Inorganic Ions (μeq/l), Conductivity (μS/cm) and Metals (ng/l) Found in Bulk Precipitation Samples Collected in Eleven Sampling Sites Located in the Metropolitan Area of Costa Rica, August–November, 2007.

Concentration (μequl^{-1})	Sampling Sites										
	San Jose					Heredia				BELEN	
	BN-SJ	MSP-SJ	SP-MSJ	MSJ-SJ	ICE-SJ	REC-HE	ILA-HE	MEC-HE	CBN-HE	ZI-BE	CCLR-BE
Cl^-	9 ± 8	8 ± 6	6 ± 3	13 ± 11	5 ± 8	5 ± 4	14 ± 11	6 ± 5	5 ± 1	6 ± 4	6 ± 8
NO_3^-	3 ± 1	4 ± 5	3 ± 2	4 ± 3	3 ± 2	3 ± 3	3 ± 2	3 ± 1	3 ± 0,9	2 ± 1	2 ± 1
SO_4^{2-}	61 ± 28	56 ± 27	48 ± 25	56 ± 22	43 ± 41	72 ± 49	55 ± 26	59 ± 24	40 ± 11	42 ± 25	43 ± 20
Na^+	15 ± 0,4	10 ± 5	13 ± 14	12 ± 5	11 ± 6	14 ± 8	10 ± 7	22 ± 7	15 ± 5	10 ± 8	12 ± 5
NH_4^+	20 ± 15	12 ± 3	8 ± 16	20 ± 23	14 ± 19	15 ± 12	22 ± 8	26 ± 11	12 ± 19	8 ± 8	8 ± 11
K^+	8 ± 4	6 ± 3	10 ± 6	8 ± 7	nd	4 ± 2	7 ± 3	nd	nd	4 ± 1	10 ± 14
Ca^{2+}	16 ± 31	8 ± 31	7 ± 12	16 ± 9	nd	21 ± 38	21 ± 10	nd	nd	7 ± 3	7 ± 5
H^+	15 ± 13	37 ± 27	25 ± 22	23 ± 20	28 ± 26	26 ± 18	14 ± 15	15 ± 13	26 ± 22	25 ± 26	19 ± 18
Metals (ngl^{-1})											
V	4,0 ± 0,6	2,0 ± 0,5	2,0 ± 0,8	1,0 ± 0,5	1,0 ± 0,1	1,0 ± 0,8	2,0 ± 0,5	2,0 ± 0,5	2,0 ± 0,5	4 ± 1	3,0 ± 0,7
Pb	5 ± 1	3 ± 2	4 ± 2	3 ± 2	1,0 ± 0,7	3 ± 2	3 ± 2	2,0 ± 0,4	3 ± 1	5 ± 1	6 ± 2
Cr	4,0 ± 0,8	2 ± 1	3 ± 1	1,0 ± 0,6	2,0 ± 0,5	2 ± 2	3 ± 1	2,0 ± 0,6	3,0 ± 0,9	3,0 ± 0,8	4,0 ± 0,7
Cu	4 ± 2	4 ± 3	5 ± 1	4 ± 2	2,0 ± 0,8	7 ± 5	5 ± 2	3,0 ± 0,7	7 ± 2	16 ± 4	12 ± 3
Ni	3,0 ± 0,4	2 ± 1	2,0 ± 0,4	1,0 ± 0,4	0,7 ± 0,4	2,0 ± 0,6	0,9 ± 0,5	2,0 ± 0,5	2,0 ± 0,4	2,0 ± 0,6	4,0 ± 0,8
Mn	16 ± 6	20 ± 8	20 ± 6	14 ± 7	4 ± 2	21 ± 6	22 ± 9	6 ± 3	16 ± 4	19 ± 6	24 ± 6
Al	354 ± 116	324 ± 72	322 ± 56	309 ± 79	228 ± 72	577 ± 63	468 ± 76	334 ± 46	302 ± 37	413 ± 83	531 ± 72
Fe	58 ± 14	54 ± 14	52 ± 11	60 ± 16	30 ± 8	127 ± 14	77 ± 15	38 ± 12	37 ± 8	88 ± 9	113 ± 19
Conductivity (μScm^{-1})	15 ± 14	18 ± 8	13 ± 6	17 ± 9	14 ± 12	14 ± 6	14 ± 9	12 ± 6	12 ± 4	16 ± 8	14 ± 7

The value indicated as ± represents the volumen weigthed standard deviation of the data. (nd = not detectable).

at the same concentration level, in the lineal range of the method and analyzed for both soluble ions and metals. The result of bias and precision for each ion and metal analyzed was included in Table **5**.

3. RESULTS AND DISCUSION

3.1. Chemical Composition

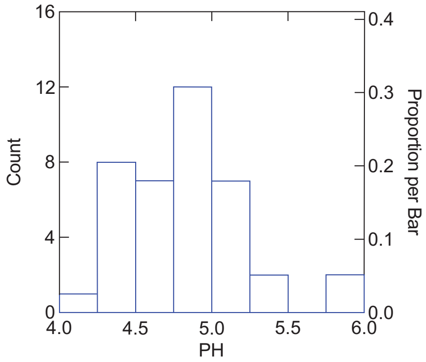
Table **6** shows volume-weighted average and standard deviations values obtained for conductivity, inorganic ions and metals in bulk precipitation samples collected at the 11 sampling sites.

Fig. (**2a-c**) shows the frequency distribution and the event variation of pH of the bulk precipitation in three different sites located in the metropolitan area of Costa Rica in August – December 2007. As the pH of the unpolluted natural water in equilibrium with atmospheric CO_2 is 5.6, the rainwater, in which the pH is less than 5.6, is considered to be acid rain [12]. It could be seen clearly that in REC-HER (commercial zone with high vehicular flux) there were 87% events of bulk precipitation measured, in which the pH values were less than 5.6. 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. 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.

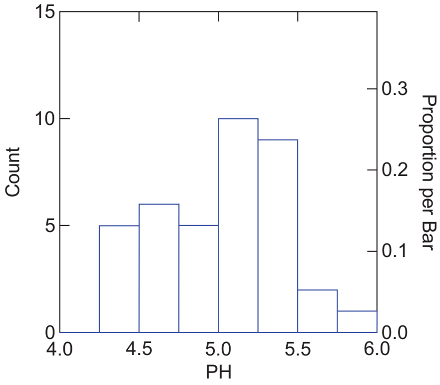
Table **7** shows the Spearman correlation coefficient matrix of the trace metals and ion species present in total precipitation. Three ion species (K^+, Cl^- y Na^+) show significant correlation coefficients due to their predominantly marine origins. The relationship between H^+ y Cl^- ions is not significant, 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-} y 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 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 (Seinfield and Pandis, 1998).

Principal component analysis was a multivariate statistics technique applied to qualitatively identify the sources of chemical composition in individual bulk precipitation events [13, 14]. In order to further identify the sources of the ionic and metallic constituents in the bulk precipitation samples, principal component analysis was performed in this study.

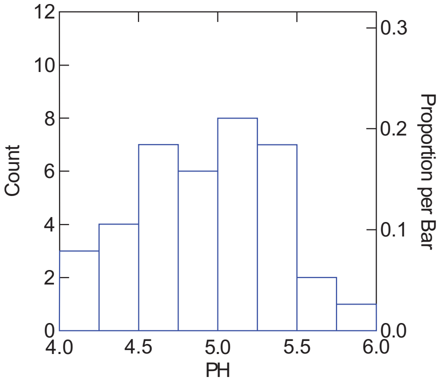
Table **8** showed the varimax-rotated principal component patterns for bulk precipitation data (including all the sampling sites). Three major factors whose eigenvalues were greater than 1 was extracted accounting for 91.0% of the total variance with significant factor loadings greater than 0.6. PC1 has high loadings for NO_3^-, SO_4^{2-} and NH_4^+, which was associated with the secondary aerosol source, such as the chemical transformation of SO_2, NOx on the surface of the aerosols. PC2 has high loadings for Cl^-, Na^+, and K^+, which was likely associated with the marine aerosol. In PC3 there was a high loading for pH, moderate loadings for Ca^{2+} and Mg^{2+}, and weak loadings for other ions. PC3 was likely associated with the soil as a source.



(a) REC-HE



(b) MEC-HE



(c) CCLR-BE

Fig. (2). PH frequency distribution of the bulk precipitation in the different sites located in the Metropolitan area of Cost Rica.

The ions in bulk precipitation were mainly from anthropogenic sources, sea spray and terrestrial dust from wind erosion, provided that contributions from volcanic and other natural sources were negligible. The chemical compositions of bulk precipitation were expected to reflect the relative contribution of the ions from these reservoirs [15, 16].

The anthropogenic, marine and crust sources of ionic components in rainwater were computed respectively using the following equations [17]:

%SSF = 100 (X/Na^+) marine/(X/Na^+) bulk precipitation

%CF = 100 (X/Ca^{2+})soil/(X/Ca^{2+}) bulk precipitation

%AF = 100 - %SSF - %CF

where SSF, CF and AF represented sea spray fraction, crust fraction and anthropogenic fraction, respectively. Table **9** showed the approximate contributions of different sources to ionic species in bulk precipitation. The results indicated that nearly all the SO_4^{2-}, Ca^{2+} and K^+ appeared to be of non-marine origin. Ca^{2+} and K^+ were mainly from crust origin. K^+ might be also considered as a chemical signature of biomass burning [17]. K^+ occurs usually in coarse particles in soil, while fine particles of K^+ resulted from the wood burning.

Bulk 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 bulk precipitation acidity, fractional acidity (FA) can be calculated as [18]:

$$FA=\frac{[H+]}{([\text{nss}\,SO_4^{-2}]+[NO_3^-])} \qquad (1)$$

If this ratio is one, acidity generated by strong acids is not completely neutralized. Fig. (**3**) shows the differences in fractional acidity of bulk 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^-] + [nss SO_4^{-2}]), resulting in a value between 0.045 and 0.055, showing that approximately 4.5 to 5.5% of the total acidity of bulk precipitation is due to NO_3^-, while 95–96.5% of acidity can be attributed to SO_4^{2-}.

The application of Multiple Linear Regression Analysis showed the relationship between the anions SO_4^{2-}, NO_3^- and the cations Ca^{2+}, NH_4^+ and H^+ as independent variables (Table **10**). The results suggest that NH_4^+ is the major neutralizing agent for both SO_4^{2-} and NO_3^-, while the site REC-HE showed a higher Ca^{2+} contribution that could be attributed to major concentration of basic species in particulate matter PM10 predominant in this site. On the other hand, Ca^{2+} appears to play a significant role in the neutralization process, where 27.7 - 36.1% of SO_4^{2-} and 22.5-37.9% of NO_3^- are in the form of $CaSO_4$ and $Ca(NO_3)_2$ respectively. The remarkable association of nitrates with H+ indicates that 1.3-7.0% of HNO_3 was not neutralized by

Table 7. Spearman Correlation Coefficient for Inorganic Ions and Metals Present in Samples of Bulk Precipitation, Collected in the Metropolitan Area of 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^+	**0.757**	0.082	0.341	1.000											
NH_4^+	0.318	**0.573**	**0.707**	0.470	1.000										
K^+	**0.693**	-0.062	-0.073	**0.506**	0.287	1,000									
H^+	0.112	**0.521**	**0.589**	-0.063	0.111	-0.239	1.000								
V	0.019	-0.034	**0.483**	0.285	**0.488**	-0.163	0.288	1,000							
Pb	-0.140	-0.068	**0.540**	0.152	-0.126	0.208	-0.315	**0.583**	1.000						
Cr	0.315	0.101	-0.100	0.195	0.120	0.007	-0.033	0.104	0.044	1.000					
Cu	0.015	0.106	**0.485**	-0.318	-0.147	-0.156	0.132	0.029	**0.493**	-0.217	1.000				
Ni	-0.143	0.111	0.152	0.137	0.080	0.156	-0.096	0.150	**0.611**	0.173	**0.478**	1,000			
Mn	-0.072	**0.472**	0.249	-0.155	**0.539**	0.211	0.210	**0.570**	**0.504**	-0.035	0.072	**0.507**	1,000		
Al	-0.037	0.147	0.118	0.067	0.221	0.294	0.121	0.206	0.201	-0.006	0.102	**0.556**	**0.595**	1,000	
Fe	-0.251	0.057	-0.146	-0.352	-0.190	-0.117	0.293	0.038	-0.116	0.128	0.197	0.058	0.146	0.076	1,000

Values in **bold** are significant at a $p < 0.05$, n= 38.

calcium compounds (as $CaCO_3$) and NH_3, while a small percentage (4.7%–11.5%) of $SO_4{}^{2-}$ is in the form of H_2SO_4.

Table 8. Factor Analysis of All Evaluated Variables of Bulk Precipitation Samples Collected in the Metropolitan Area of Costa Rica, August-November 2007

	F1	F2	F3
Cl^-	-0.019	**0.914**	0.144
NO_3^-	**0.838**	0.025	-0.094
SO_4^{-2}	**0.788**	0.336	0.220
Na^+	0.138	**0.778**	0.346
NH_4^+	**0.683**	0.307	0.091
Ca^{+2}	0.072	0.172	**0.646**
Mg^{+2}	0.156	0.263	**0.720**
K^+	-0.269	**0.814**	-0.561
H^+	**0.636**	-0.113	**0.896**
V	-0.174	0.172	0.111
Pb	-0.134	-0.143	0.306
Cr	0.003	0.277	-0.200
Cu	-0.026	-0.169	-0.030
Ni	0.137	-0.111	0.012
Mn	0.304	-0.027	0.206
Al	0.035	0.032	0.161
Fe	0.060	-0.446	0.556
Eigen values	2.545	2.213	1.659
Percentage of total variance	34.7	29.9	22.7
Possible source	Neutralization	Marine aerosol	Crustal

Bold numbers represent factor loading values significatives.

The equivalent ratio of $(Ca^{2+} + NH_4^+)/(SO_4^{2-} + NO_3^-)$ could be used as an index for evaluating the degree of the anthropogenic activity [19]. In the bulk precipitation samples of Heredia, the ratio of $(Ca^{2+} + NH_4^+)/(SO_4^{2-} + NO_3^-)$ was 0.67, the highest among the three cities, and Heredia had one of the lowest acidification, as the pH of the rainwater was in the alkaline range, which was only because of the neutralization of the basic cations. In contrast, the ratio of $(Ca^{2+} + NH_4^+)/(SO_4^{2-} + NO_3^-)$ in the bulk precipitation of both San José (0.30) and Belen (0.35) were much lower than Heredia, indicating that both San Jose and Belen were heavily affected by anthropogenic air pollution. The high concentrations of SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, Ca^{2+} and H^+, in the bulk precipitation would have a great impact on the hydrobiological system on the surface of the earth on both local and regional scales and have attracted extensive concern, as the wet deposition participates actively in the balance of the air–water–soil system [20].

3.2. Effect of Aerosol Composition

The average and the standard deviation of both valid data concentration of PM_{10} particles and its main constituents, for each of the sampling site, are presented in Table **11**. For all the sampling sites, the predominants ions were SO_4^{2-} and Na^+ followed by Cl^-, PO_4^{3-}, NH_4^+ y NO_3^- for those with high vehicular flow (CAT-SJ, CCLR-BE, REC-HE) while for sites in transition from commercial to residential area, the concentration of PO_4^{3-} turned out to be greater than that of Cl^-. Ionic constituents represent 22.0, 20.0, 14.6, 20.8 and 15.7% of total mass of PM_{10}, collected in the sampling sites of CAT-SJ, JE-SJ, REC-HE, GOB-HE and CCLR-BE respectively. In the case of heavy metals, Fe, Al, Mn and Cu concentrations were greater in PM_{10} while Cr and Ni were the less abundant species, with the exception of the sampling sites located in Heredia city, where Cr showed higher levels to those found in other places.

Table 9. Source Contributions for Different Ionic Constituents in Bulk Precipitation Measured in Metropolitan Area of Costa Rica, 2007

Sampling Site	MSJ-SJ			REC-HE			CCLR-BE		
Ion	%SSF	%CF	%AF	%SSF	%CF	%AF	%SSF	%CF	%AF
SO_4^{2-}	1.50	0.24	98.50	1.16	0.23	98.61	1.67	0.13	98.20
Cl^-	79.5	0.22	20.31	99.99	0.01	-	99.80	0.20	-
Ca^{2+}	0.45	99. 55	-	3.37	96.63	-	8.67	91.33	-
K^+	1.94	51.57	46.48	4.53	81.65	13.82	1.55	58.05	40.40
Na^+	99.35	0,65	-	99.90	0.10	-	99.93	0.07	-
NO_3^-	-	0.30	99.70	-	0.47	99.53	-	0.24	99.76

Table **12** shows the Spearman correlations between some ionic species in PM_{10} and bulk precipitation. There was a negative correlation of pH value with PM_{10}. As pollution aerosols, such as SO_4^{2-} and NO_3^- that mostly exist in finer particles are the major contributors to acidity while they are scavenged into rainwaters [21,22]. As shown in Table **11**, are significant correlations between $Na^+{}_{PM10}$ - $Na^+{}_{bp}$, $Cl^-{}_{PM10}$ - $Cl^-{}_{bp}$, $K^+{}_{PM10}$ - $Cl^-{}_{bp}$ and $K^+{}_{PM\ 10}$ - $Na^+{}_{bp}$, which relate the significant contribution of the marine aerosol to chemical composition of the bulk precipitation samples. It should be noted, as expected, the resulting negative correlation between acidic species present in the particles with respect to the pH of bulk precipitation and similarly, the inverse relationship with respect to the basic ions.

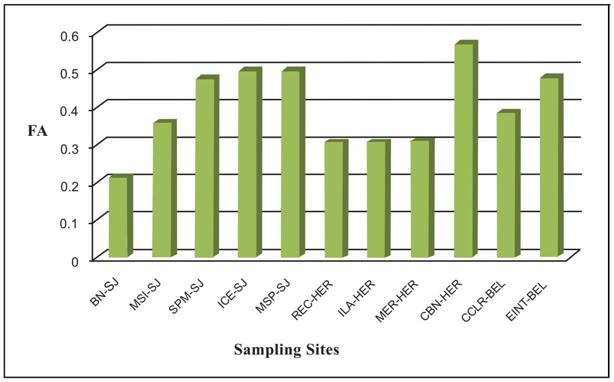


Fig. (3). Variation of fractional acidity in bulk precipitation samples collected in sampling sites of the Metropolitan area of Costa Rica, 2007.

The cross correlation between the ions in PM_{10} concentrations on samples obtained from bulk precipitation. Fig. (**4**), shows that the acidic species (SO_4^{2-} and NO_3^-) have significant positive correlations with respect to the bulk precipitation with a lag of 3 to 4 days while the basic species (Ca^{2+}, Na^+, K^+) show a similar behavior only with a lag of 0 to 1 days, why would appear that the removal of particles by means of bulk precipitation tends to occur more rapidly for ions of basic character than those of acidic nature. This behavior can be explained due to increased water solubility of the basic ions.

The heavy metal concentrations of bulk precipitation and PM_{10} samples were compared over the common observation period. This study supports other reported observations that precipitation events can strongly influence variability in concentrations of particles samples [19, 20, 25]. Correlation analyses between the heavy metal concentrations in bulk precipitation and particles samples was performed in order to determine if there was any discernible statistical relationship between the two types of samples. The only statistically significant relationship that has been reported for ambient air and wet deposition samples was observed between content of Mn with a correlation coefficient (r^2) of 0.71, p= 0.001. On the other hand cupper, chromium, and lead for the same period showed weaker correlation which is 0.12, 0.27 and 0.10, respectively.

Table 10. Multiple Linear Regression Data for SO_4^{2-} and NO_3^- Against Ca^{2+}, NH_4^+ and H^+ According to the Equations

$$[SO_4{}^{2-}] = \alpha_0 + \alpha_1[Ca^{2+}] + \alpha_2\,[NH_4^+] + \alpha_3\,[H^+]$$
$$[NO_3{}^-] = \beta_0 + \beta_1[Ca^{2+}] + \beta_2\,[NH_4^+] + \beta_3\,[H^+]$$

Independent Variables	MSJ-SJ	REC-HE	CCLR-BE
SO_4^{2-}			
% explained by $[Ca^{2+}]$	27.7	36.1	30.5
% explained by $[NH_4^+]$	58.6	65.4	60.2
% explained by $[H^+]$	11.5	4.7	7.1
NO_3^-			
% explained by $[Ca^{2+}]$	22.5	37.9	27.9
% explained by $[NH_4^+]$	64.8	61.3	57.3
% explained by $[H^+]$	7.0	1.3	3.2

3.3. Effect of Rainfall Volume

The volume of precipitated water is a variable that influence the chemical composition of bulk precipitation samples. As noted in Fig. (**5**), the concentration of ionic species in bulk precipitation samples, decreases logarithmically with increasing amount of water precipitated during sampling. The ion H^+ is the exception to this behavior, because its concentration increases with increasing the volume of rainfall. The logarithmic relationship between the concentrations of some chemical species present in the total deposition and the volume of precipitated water have been reported in numerous studies [23, 24, 25]. These authors agree that this behavior of decreasing concentrations with increasing rainfall volume is the product precipitated as

Table 11. Average Concentrations of Inorganic Ions (μgm^{-3}) and Metals (ngm^{-3}) Found in PM_{10} Collected in Five Sampling Sites Located in Metropolitan Area of Costa Rica, August -December 2007

Concentration (μgm^{-3})	San Jose		Heredia			Average
	CAT-SJ	JE-SJ	REC-HE	GOB-HE	CCLR-BE	
PM_{10}	46 ± 13	31 ± 6	58 ± 14	33 ± 10	41 ± 8	**42**
F^-	0,14 ± 0,07	0,09 ± 0,05	0,07 ± 0,03	0,08 ± 0,01	0,10 ± 0,08	**0,10**
Cl^-	0,99 ± 0,64	0,59 ± 0,43	0,63 ± 0,36	0,45 ± 0,29	0,49 ± 0,30	**0,63**
NO_3^-	0,29 ± 0,15	0,15 ± 0,08	0,19 ± 0,09	0,22 ± 0,10	0,17 ± 0,07	**0,20**
PO_4^{-3}	0,83 ± 0,57	0,64 ± 0,47	0,51 ± 0,38	1,12 ± 0,55	0,37 ± 0,22	**0,69**
SO_4^{-2}	4,9 ± 2,3	2,8 ± 1,2	3,4 ± 1,2	2,6 ± 0,8	3,3 ± 0,9	**3,4**
Na^+	1,2 ± 0,6	0,77 ± 0,45	2,4 ± 2,4	1,6 ± 1,5	1,1 ± 0,5	**1,4**
NH_4^+	0,55 ± 0,57	0,36 ± 0,41	0,59 ± 0,31	0,31 ± 0,25	0,32 ± 0,28	**0,43**
K^+	0,47 ± 0,53	0,28 ± 0,29	0,26 ± 0,13	0,16 ± 0,09	0,25 ± 0,11	**0,28**
Mg^{+2}	0,10 ± 0,06	0,06 ± 0,03	0,10 ± 0,04	0,08 ± 0,04	0,09 ± 0,05	**0,09**
Ca^{+2}	0,68 ± 0,51	0,35 ± 0,17	0,39 ± 0,26	0,24 ± 0,13	0,24 ± 0,25	**0,38**
Metals (ngm^{-3})						
V	5,6 ± 5,2	5,4 ± 5,8	2,9 ± 1,3	3,3 ± 1,1	22,9 ± 9,9	**8,0**
Pb	12 ± 15	14 ± 12	4,1 ± 1,2	3,8 ± 1,8	5,6 ± 2,2	**7,8**
Cr	0,86 ± 0,80	0,72 ± 0,50	5,8 ± 2,8	5,9 ± 3,1	3,9 ± 2,2	**3,4**
Cu	17,2 ± 5,2	15,1 ± 6,1	51 ± 22	66 ± 63	364 ± 105	**103**
Ni	2,22 ± 0,83	2,22 ± 0,89	1,40 ± 0,86	1,72 ± 0,55	6,9 ± 2,3	**2,9**
Mn	32 ± 19	27 ± 16	54 ± 30	45 ± 17	48 ± 24	**41**
Al	543 ± 390	232 ± 159	453 ± 233	339 ± 148	567 ± 146	**427**
Fe	471 ± 184	326 ± 68	535 ± 189	418 ± 194	621 ± 143	**474**

The value indicated as ± represents the standard deviation of the data.

washing the atmosphere below the clouds and the evaporation of raindrops during the early stages of the event of rain. In the case of H^+, this ion tends to increase due to the decrease in the concentration of ions like NH_4^+ and Ca^{2+} which function to neutralize the acidity present.

Table 12. Spearman Correlation Coefficients Between Major Chemical Species Present in PM_{10} and with Respect to the Bulk Precipitation Samples

	Cl^- bp	NO_3^- bp	SO_4^{-2} bp	Na^+ bp	pH	CE
PM_{10}	-0,231	0,034	-0,086	0,040	-0,417	0,152
Cl^-_{PM10}	**0,518**	-0,072	0,038	0,250	0,038	-0,220
$NO_3^-{}_{PM10}$	-0,217	0,094	-0,009	0,191	-0,081	-0,090
$SO_4^{-2}{}_{PM10}$	-0,286	-0,029	-0,138	0,036	**-0,436**	-0,216
Na^+_{PM10}	0,419	-0,040	0,181	**0,614**	-0,025	0,059
Ca^{+2}_{PM10}	-0,052	-0,024	0,065	0,146	**0,450**	0,148
Mg^{+2}_{PM10}	-0,217	0,055	-0,041	-0,067	**0,413**	-0,030
K^+_{PM10}	**0,483**	0,064	0,420	**0,567**	0,304	0,072
$NH_4^+{}_{PM10}$	-0,099	0,004	-0,209	-0,019	0,216	0,045

The numbers in **bold** represent significant correlations at $p < 0.05$, $N = 44$.

Other variables that may affect the chemical composition of the bulk precipitation are the total dry period preceding the rain event and the volume of rainfall in the previous event. In analyzing the effect of dry period prior to the event of rain on the chemical composition of bulk precipitation samples was found a strong positive correlation for all ions except H^+ (Table **13**), this observation has been reported by others authors [26, 27]. This phenomenon can be partly attributed to two situations: first because higher dry deposition rates tend to occur during periods of no rain and second to the contribution of wet deposition to total precipitation enriches the concentration of ions increased atmospheric wash in the first rains after dry periods.

3.4. Wind Direction and Velocity

The influence of the origin of air masses on the chemical composition of bulk precipitation has been demonstrated in numerous studies [28, 29, 30]. To analyze the effect of speed and wind direction on concentrations of ions and metals in bulk precipitation samples, wind directions were categorized into four groups. The first group of 0 to 90 °, the second from 90 to 180 °, the third from 180 to 270 ° and the fourth from 270 to 360 °. Figs. (**6**, **7**) are shown the average concentration of metals and ions according to the quadrant for some monitoring sites. For the sampling sites located in the city of San Jose, prevailing wind directions are first southwest at around 75 - 50% of the time and southeast, mostly. The concentrations of the chemical species present in bulk precipitation samples were found to be higher when air masses move in a southeasterly direction, probably due to the concentration of industrial activities in this sector of the city compared with residential areas located southwest of San Jose.

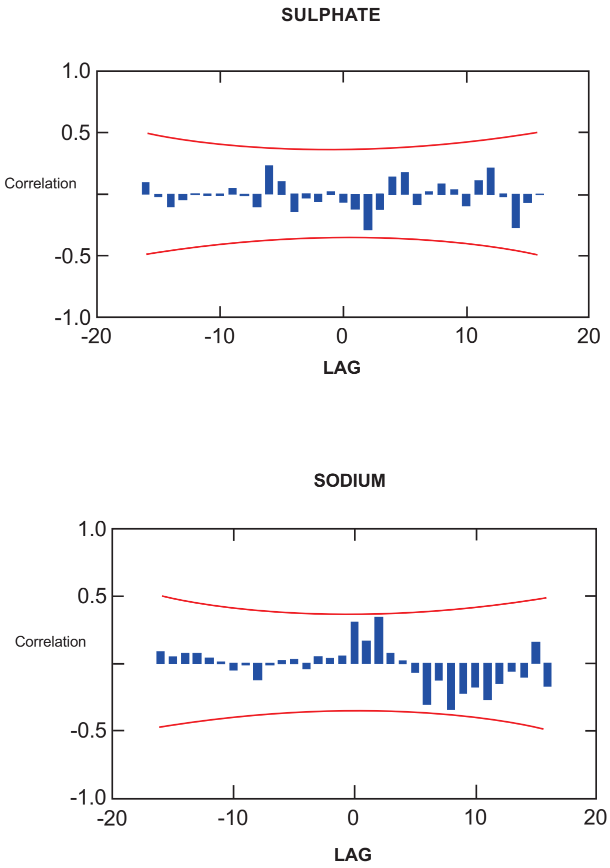


Fig. (4). Diagrams of cross correlation between ionic species in PM10 and bulk precipitation in the City of San Jose, August-November 2007.

In additionally, it is worth noting that concentrations of ionic species in bulk precipitation samples were found to be higher at wind speeds <1.5 ms^{-1}. This can be explained by the fact that the winds decrease the removal of gases and particles in the sampling sites is lower, allowing a greater leaching during rains.

The sampling sites located in the cities of Heredia and Belen, are located to the NE and NW of the metropolitan area, respectively, in the direction of air masses from the City of San Jose. For these six samples collection sites were presented addresses prevailing winds from the southeast and southwest, exclusively. According to what was observed in both cities, the highest concentrations are presented for the second quadrant (E-SE), especially for ionic species, as in the case of concentrations of metals are found to be significantly different at a level of 5% significance.

The principal component analysis can be used to study the diferent sources that contributes with the variations of the concentration of ionic species in bulk precipitation samples in 11 sampling sites located in the metropolitan area of Costa Rica. Some authors have used this statistical tool to distinguish between local and large scale phenonmena in the analysis of air pollution [31]. Aditionally, these results can be used to validate the classification of the monitoring sites.

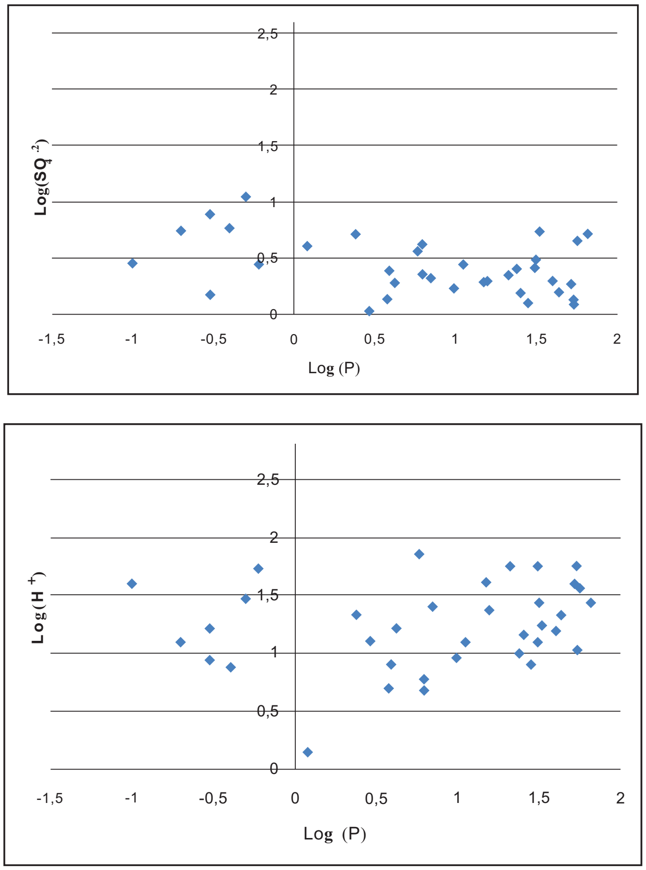
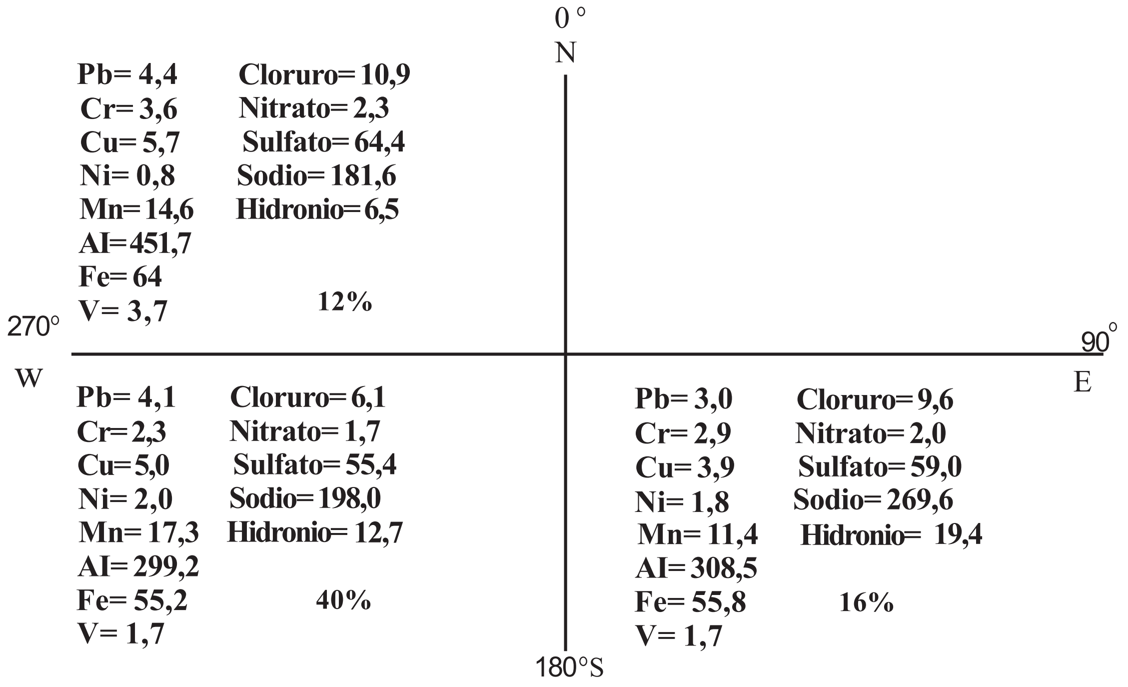


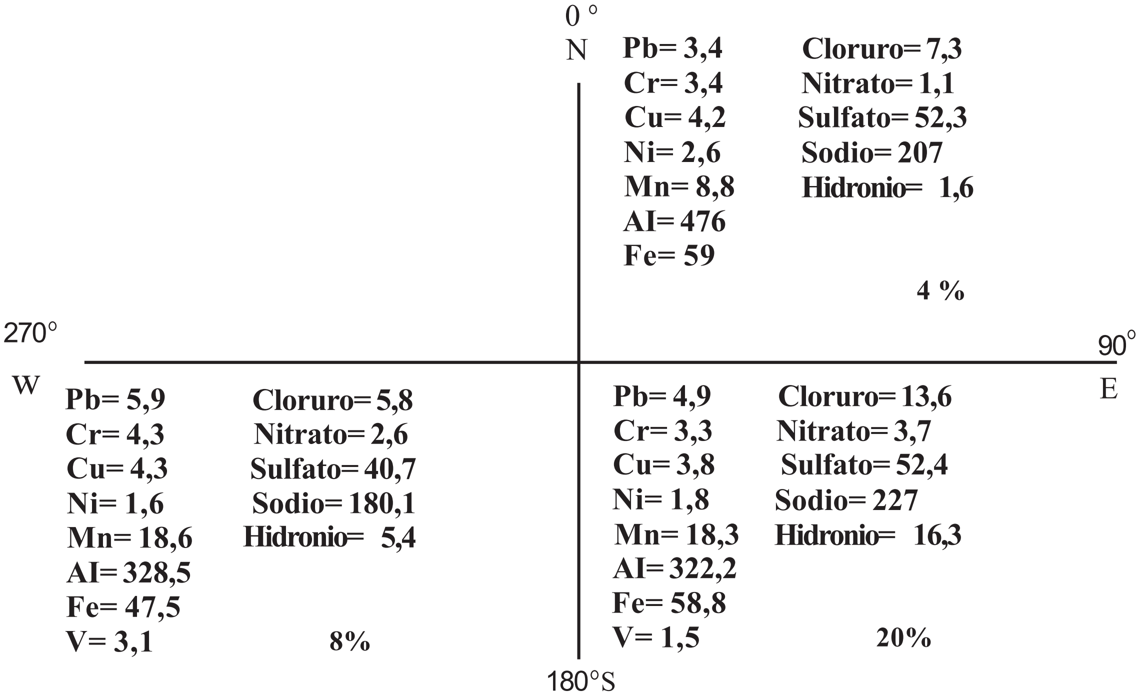
Fig. (5). Relationship between the logarithm of the concentration of ionic species in bulk precipitation samples collected at the Rectory UNA, Heredia (August-November 2007) with respect to the logarithm of the amount of water precipitated during sampling.

Table 13. Spearman Correlation Coefficients Between the Dry Periods Before the Rains and the Chemical Composition of Bulk Precipitation Samples Collected in the Metropolitan Area of Costa Rica, August-November 2007

Sampling Sites	Cl^-	SO_4^{-2}	Na^+	H^+
BN-SJ	0,472	0,444	0,656	0,006
MSJ-SJ	0,545	0,480	0,573	0,097
SPM-SJ	0,521	0,511	0,506	0,008
ICE-SJ	0,389	0,421	0,499	-0,234
MSP-SJ	0,487	0,430	0,517	-0,195
REC-HER	0,537	0,493	0,694	-0,234
ILA-HER	0,562	0,514	0,639	0,044
MER-HER	0,604	0,580	0,592	0,011
CBN-HER	0,528	0,172	0,488	-0,129
CCLR-BEL	0,495	0,287	0,439	0,179



Wind Speed < 1,5 m/s



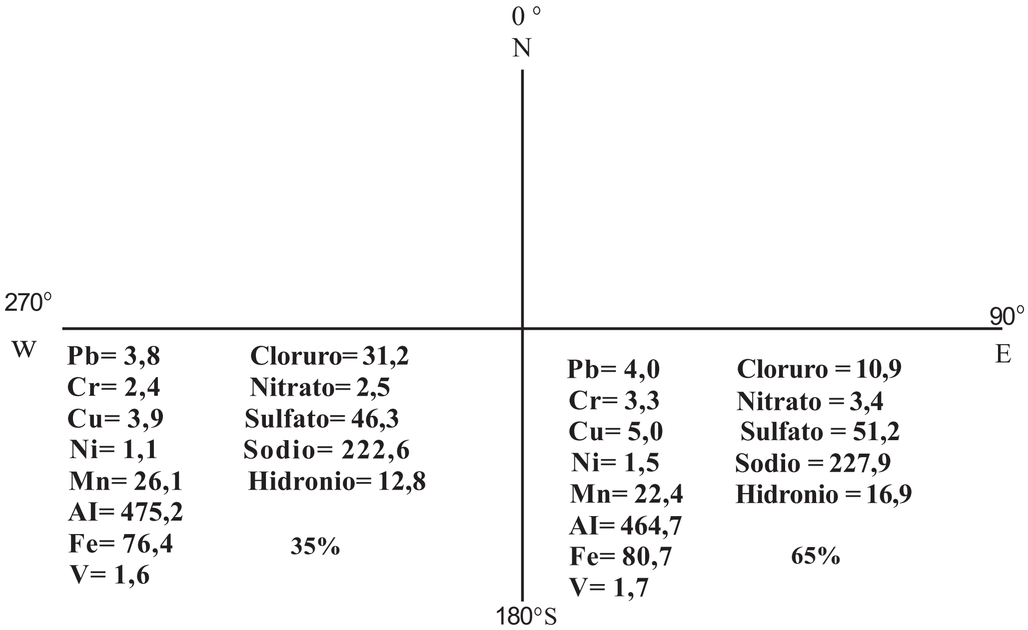
Wind Speed > 1,5 m/s

Fig. (6). Relationship between wind trajectories recorded in the National Library, San Jose and the chemical composition of precipitation samples collected.

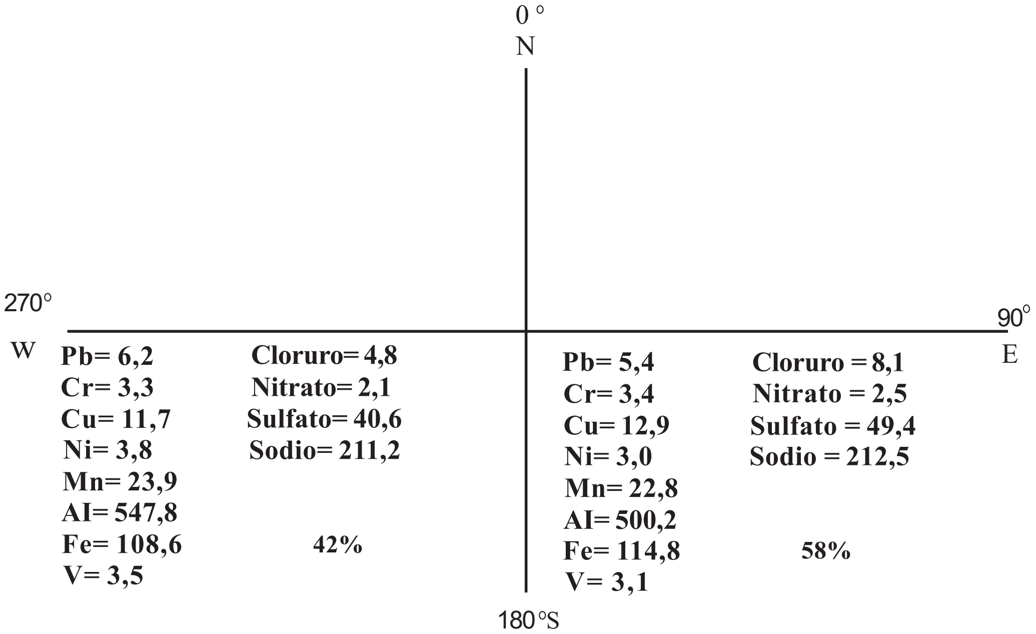
EINT-BEL	0,361	0,410	0,503	-0,031

The numbers in **bold** represent significant correlations at $p < 0.05$, N = 44.

Table **14** shows the results of principal component analysis for the 11 sampling sites using data from the concentration of SO_4^{-2} present in bulk precipitation samples. The high percentage of variance explained by the first principal component (58%) shows that variations in the



a) ILA-HE



b) CCLR-BE

Fig. (7). Relationship between wind trajectories recorded at two monitoring sites and the chemical composition of precipitation samples collected.

concentrations of SO_4^{-2} for the different sites are strongly correlated (phase concentration changes). This indicates that changes in concentration are mainly determined by large-scale phenomena (meteorological). The second component shows negative or small positive values for the sampling sites located in the northeast and northwest of the metropolitan area in relation with the others sites, which may indicate the presence of a large-scale gradient southwest-northeast. That is according with the industrial patron distribution in the area. The third principal component shows a correlation between the sampling sites located in areas of high traffic flow, it can indicate the influence of the mobile sources emissions.

Table 14. Results of Principal Component Analysis for data SO_4^{-2} Concentrations in Bulk Precipitation Samples Obtained for the Sampling Sites

	PC1	PC2	PC3
Explained Variance	58,0 %	22,5%	11,8%
Factors with components < 0			
		ILA-HER -0,106 MERC-HER -0,045	BN-SJ -0,085 MERC-HER -0,112
Factors with components > 0			
	Large: MSJ-SJ 0,865 REC-HER 0,939 MER-HER 0,814 CCLR-BEL 0,549 **Small:** CBN-HER 0,269 BN-SJ 0,188	**Large:** ICE-SJ 0,889 MSP-SJ 0,956 **Small:** REC-HER 0,457 CCLR-BEL 0,337 EINT-BEL 0,192	**Large:** CBN-HER 0,823 MSP-SJ 0,756 SPM-SJ 0,531 **Small:** MSJ-SJ 0,089 ICE-SJ 0,104 REC-HER 0,130

CONCLUSIONS

The analysis of almost all of the bulk precipitation samples collected in the metropolitan area of Costa Rica showed that: (1) the scavenging of the pollutants from the air affected directly and greatly the pH and the composition of the bulk precipitation in the metropolitan area. (2) The major ions and their concentrations in bulk precipitation followed the order of: $SO_4^{2-} > NH_4^+ > Ca^{2+} > Na^+$. (3) SO_4^{2-} and NO_3^- were the major acidifying ions in bulk precipitation samples. Ca^{2+} and NH_4^+ were the predominant basic ions in buffering and neutralizing the acidity in bulk precipitation. (4) The correlation of the acidity in bulk precipitation with the concentrations of PM_{10} in the atmosphere showed that the acidity and composition in rainwater were mainly determined by the scavenging processes of those particles in the air. (5) Some meteorological factors like wind direction and velocity can determined the chemical composition of the bulk precipitation in the metropolitan area of Costa Rica.

ACKNOWLEDGMENT

None declared.

CONFLICT OF INTEREST

None declared.

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Received: October 10, 2011 Revised: November 10, 2011 Accepted: November 11, 2011