Chemical Composition and Sources of PM$_{10}$ Particulate Matter Collected in San José, Costa Rica

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Abstract: Measurements of trace metals and inorganic ions were carried out on PM$_{10}$ aerosols sampled at two sites in the city of San Jose, Costa Rica. Samples were collected with a Thermo Andersen high volume PM$_{10}$ sampler on glass fiber and quartz filters. The ions SO_4^{2-}, NO_3^-, Cl^-, F^-, PO_4^{3-}, NH_4^+, K^+, Na^+, Ca^{2+} and Mg^{2+} were analyzed by ion chromatography and the trace metals V, Cu, Cr, Pb, Ni, Mn, Fe and Al were analyzed using an atomic absorption spectrometer with a graphite furnace attachment. The results indicated that SO_4^{2-} was the most abundant ion, and Al the trace metal with the highest concentration.

Pearson'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 Ca^{2+}-Mg^{2+} indicated a crustal origin. No correlation was found among the trace metals except Cu-Cr and Fe-Cr. The influence of wind direction on trace metal concentrations is also discussed.

Keywords: Water soluble ions, PM$_{10}$, Trace metals, Costa Rica.

1. INTRODUCTION

The country of Costa Rica is crossed by a mountain range system running from NW to SE. The system includes many volcano cones with elevations up to 3600 m above sea level (asl), forming a central plateau known as the Area Metropolitan at 1100 m asl with an area of about 3000 km^2. This region contains 75% percent of the motor vehicles (734,200), 85% of the industry and 60% of the population (2,580,000) of the country, according to the latest census [1].

The national capital, San José, is located at 90° 56' 16" N by 84° 06' 55" W. The city has a maximum breadth of 14 km from northwest to southeast, and is the largest urban area in Costa Rica. As a result of the lack of efficient urban planning, the expansion of the city 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 µgm^{-3} in the high traffic areas of the city [2]. The presence of lead in the gasoline was eliminated since 1998.

Various studies from many parts of the world have found evidence of the harmful health effects of air pollutants and particulate matter on the human population [3-5]. However while there are epidemiological correlations between particle concentrations and health effects, it must be kept in mind that particles contain a complex and variable mix of chemical compounds that are emitted by different sources [6]. The particles toxicological properties are associated not only with size but also with toxic concentrations [7].

This study is the first PM$_{10}$ chemical composition determination to be carried out in Costa Rica, thus constituting an addition to the body of studies from other Latin American cities [8-11].

2. MATERIALS AND METHODS:

2.1. Sampling

Two sites were selected; one at the main cathedral of San Jose, 10 m from the highway and 3 m above ground level, and the second at the San Jose Board of Education building, 12 m from the main avenue and 3 m above ground (Fig. **1**).

Sampling was carried out from May 2007 to May 2008. Samples were collected 3 times a week on Mondays, Wednesdays and Fridays. For collection of the samples, two Thermo Andersen model MFC high volume samplers were used for 24 ± 1 hour daily at a flux of 1.13 ± 10% m^3/min. Every three samples, flux calibration was performed comparing the flux readings with the Variflo model 454 critical orifice pressure drop, as instructed in the manual. Pressure drop measurements were made with calibrated water manometers connected to the orifice and equipment.

For each sample, temperature and atmospheric pressure recordings were made with a Krestel 5000 anemometer.

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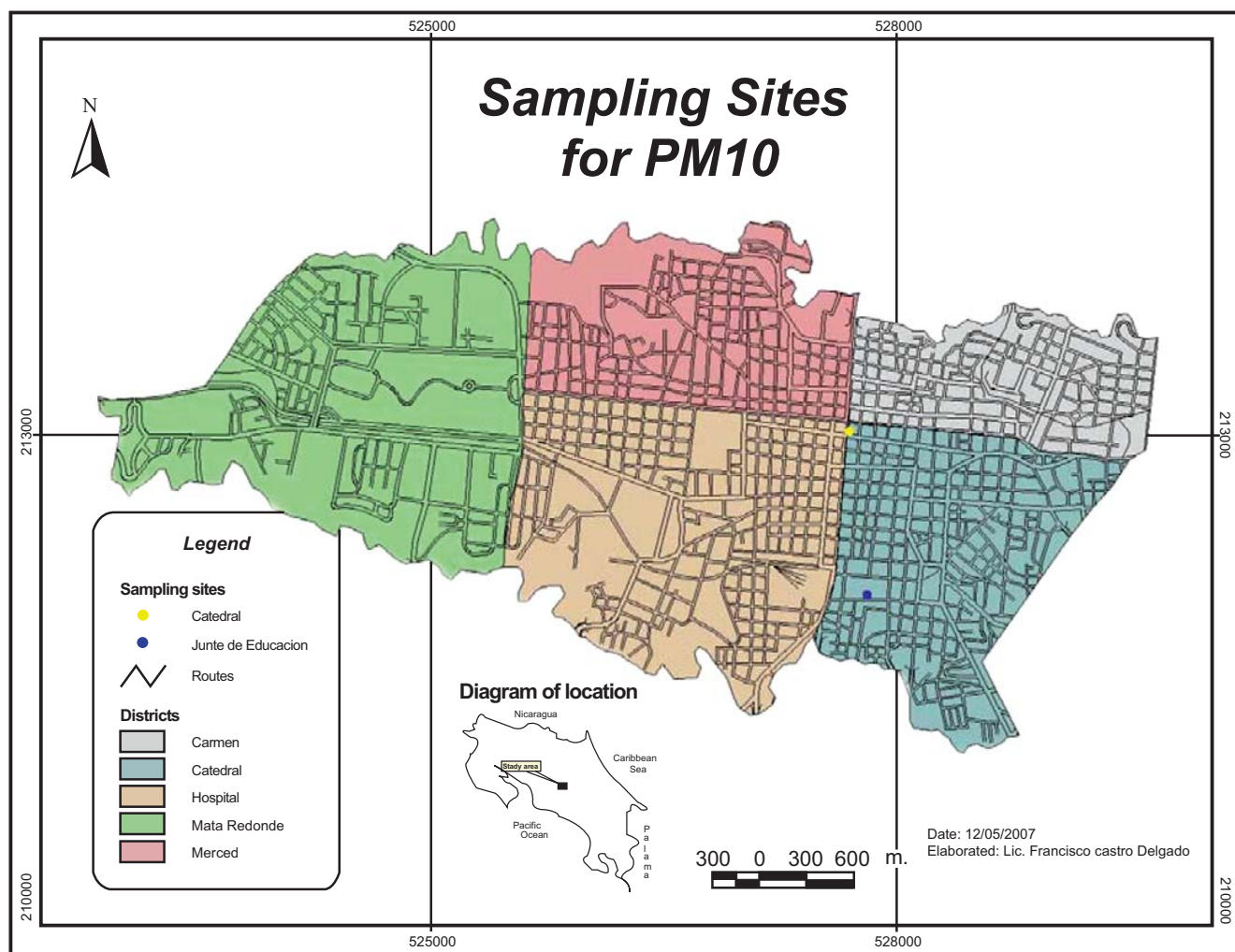
Fig. (1). Sample sites for PM$_{10}$ in San Jose City, Costa Rica.

For PM$_{10}$ collection, Whatman G653 grade glass fiber filters were used two times a week, and for heavy metal analysis, quartz filters were used once a week. Filters were conditioned for 24 h in a Nalgene Desiccator at 15-30°C at 40% R.H., and weighed before and after sampling on a Mettler analytical balance. Polyethylene zipper bags were used for filter transportation.

2.2. Analytical Methods

2.2.1. Inorganic Ions

The filters were cut into strips 2.54 cm wide by 23 cm long, and each one placed in a 150 ml beaker. 75 ml of deionized water (DW) (resistivity up to 18.2 MΩ-cm) was added and the samples were extracted in an ultrasound bath at 35°C for 60 min. The solution was then poured into a volumetric flask and filled to the mark with DW for analysis.

The inorganic ions SO_4^{2-}, NO_3^-, Cl^-, F^-, PO_4^{3-}, Ca^{2+}, Mg^{2+}, Na^+, K^+ and NH_4^+ were analyzed with a Dionex ICS-3000 high pressure liquid analyzer, quaternary pump and suppressed cartridges, as shown in Table **1**. High purity standards traceable to Merck Suprapur were used for calibration. Curves were prepared from 0.25 to 10 mg l^{-1} for anions and from 0.10 to 8.0 mg l^{-1} for cations. Calibration curves were

applied every 20 analyzed samples to observe reproducibility and retention times. Field and laboratory blanks were run using the same procedures as the samples.

In addition, detection limits, at 99.5% confidence level, were calculated with the average analytical blank concentrations plus three times the standard deviation of the blank concentrations. The results are shown in Table **2**.

2.2.2. Trace Metals

The 2.54 by 23 cm quartz fiber filter strips were put into a 150 ml beaker and 2.5 ml of ultra-pure concentrated nitric acid and 25 ml DW were added, and heated on a hot plate until almost dry. The solution remaining was poured into a 25 ml volumetric flask and DW was added up the mark. The samples were analyzed using a Perkin Elmer AAnalyst 700 spectrophotometer with a graphite furnace and automatic sampler attachments. Hollow cathode lamps were used for analysis, and a deuterium lamp for background correction.

Standards traceable to the National Institute of Standards and Technology (NIST) were used for calibration and identification. The curves were made with standard solutions from 5 to 50 µgl^{-1} for V, Cu, Cr, Ni, Fe, Pb and Al, and from 5 to

Table 1.   Analytical Instrumental Conditions for the Determination of Inorganic Ions Contained in PM$_{10}$ Particles

	Anions	Cations
Detector	Electric conductivity coupled to suppressor	Electric conductivity coupled to suppressor
Column	Dionex IonPac AS9-HC Particle size 9 µm (2 x 250 mm)	Dionex IonPac CS12A Particle size: 9 µm (2 x 250 mm)
Electric Suppressor	Dionex ASRS ULTRA II	Dionex CSRS ULTRA II
Mobile Phase	Solution of Na$_2$CO$_3$ 9 mM to pH = 10,88	Solution metanosulfonic acid 20 mM
Injection Volume	10 µl	10 µl
Flux of the mobile phase	0.25 ml/min	0.25 ml/min
Column temperature	30°C	30°C

Table 2.   Detection Limits (µg/m^3) of the Analyzed Ions

Filter	SO$_4^{2-}$	NO$_3^-$	Cl$^-$	PO$_4^{3-}$	F$^-$	Na$^+$	K$^+$	Ca^{2+}	Mg^{2+}	NH$_4^+$
Glass Fiber	0,08	0,04	0,11	0,26	0,02	0,87	0,13	0,06	0,05	0,02
Quartz	0,03	0,01	0,05	0,06	0,01	0,10	0,05	0,02	0,01	0,01

30 µgl^{-1} for Mn. Calibration curves were applied every 20 analyzed samples to observe the reproducibility of the signs.

The detection limits (µg/l) were calculated by the IUPAC [12] method and were 1.2 for V, 3.5 for Cu, 2.1 for Pb, 5.5 for Cr, 3.0 for Ni, 1.8 for Fe, and 5.6 for Al.

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 sample filters were analyzed, obtaining concentrations of less than 3% of those found in samples. The results obtained for the field blank filters 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 were spiked at the same concentration level, in the lineal range of the method, and analyzed for both soluble ions and metals. The precision found was 4.3, 4.4, 7.2, 3.6, 5.3, 4.7, 5.7 and 6.1% relative standard deviation (% RSD) for Cu, Cr, Mn, Ni, Pb, V, Fe and Al respectively. The bias, in the same order, was −0.78, 2.54, −4.7, −4.76, 0.21, −1.6, 3.2 and 4.0%. For ions, the % RSD was 3.2, 2.8, 3.7, 0.8, 1.4, 2.5, 2.1 and 3.5 for SO$_4^{2-}$, Cl$^-$, NO$_3^-$, Na$^+$, K$^+$, Ca^{2+} Mg^{2+} and NH$_4^+$. The bias, in the same order, was: 0.25, 0.63, −0.51, 1.3, −1.1, 2.4, 1.7 and 3.2%.

3. RESULTS AND DISCUSSION

3.1. Inorganic Ions and Trace Metal Concentrations

Table **3** shows the means, maximums, minimums and standard deviations of the inorganic ion concentrations for

Table 3.   Ions Average Concentrations Measured in PM$_{10}$ Particles Collected at Two Sites Located in the City of San Jose, from May2007 to May 2008

						Main Cathedral of San Jose					
Data	PM$_{10}$ (µg/m^3)	F$^-$ (µg/m^3)	Cl$^-$ (µg/m^3)	NO$_3^-$ (µg/m^3)	PO$_4^{3-}$ (µg/m^3)	SO$_4^{2-}$ (µg/m^3)	Na$^+$ (µg/m^3)	NH$_4^+$ (µg/m^3)	K$^+$ (µg/m^3)	Mg^{2+} (µg/m^3)	Ca^{2+} (µg/m^3)
Mean	47.1	0.09	0.63	0.18	0.54	3.12	0.75	0.35	0.29	0.06	0.41
Max	110.0	0.30	2.50	0.62	1.36	6.93	2.07	1.95	2.84	0.20	1.82
Min	13.0	0.03	0.09	0.07	0.06	0.81	0.21	0.03	0.01	0.02	0.03
SD	16.8	0.05	0.41	0.09	0.39	1.43	0.32	0.37	0.33	0.03	0.27
						San Jose Board of Education Building					
Datos	PM$_{10}$ (µg/m^3)	F$^-$ (µg/m^3)	Cl$^-$ (µg/m^3)	NO$_3^-$ (µg/m^3)	PO$_4^{3-}$ (µg/m^3)	SO$_4^{2-}$ (µg/m^3)	Na$^+$ (µg/m^3)	NH$_4^+$ (µg/m^3)	K$^+$ (µg/m^3)	Mg^{2+} (µg/m^3)	Ca^{2+} (µg/m^3)
Mean	29.8	0.09	0.59	0.16	0.64	2.92	0.76	0.37	0.28	0.05	0.34
Max	49.0	0.30	2.85	0.50	1.90	7.02	2.02	2.12	2.37	0.18	0.96
Min	13.0	0.03	0.03	0.04	0.07	1.20	0.23	0.02	0.03	0.02	0.10
SD	6.7	0.05	0.43	0.08	0.47	1.32	0.46	0.41	0.29	0.03	0.18

samples collected at two sites in the city of San Jose, Costa Rica from May 2007 to May 2008. The results from both sampling sites indicated that SO_4^{2-} was the most abundant ion, followed by Na^+, Cl^-, PO_4^{3-}, Ca^{2+}, NH_4^+, K^+, NO_3^-, F^-, and Mg^{2+}.

Table **4** shows the means, maximums, minimums and standard deviations of the trace metals. In this table it can be observed that Al had the highest concentrations at both sites, followed by Fe, Mn, Cu, Pb, V, Ni, and Cr.

When the results are compared with the reported for other cities it is evident that concentrations are lower than in the major cities. However, the results are higher than other cities of a similar size, e.g. Campinas, Brazil (Table **5**).

3.2. Statistical Methods

Non-parametric statistical methods were applied to all major inorganic ions and total trace metal concentrations. Non-significant differences were found between sites. The Kruskal-Wallis statistic was applied at a 5% level, confirming these results. Despite there is no significative difference in chemical composition of the particles for both sites, the Catedral Metropolitana has higher levels of PM10. This means that both sites are affected by the same sources (vehicle emissions) but the traffic flux is higher for Catedral Metropolitana.

Pearson's correlation was also applied to all inorganic ions and total trace metal concentrations. The matrix correlations are shown in Table **6**. High positive correlations were found among SO_4^{-2}, NO_3^- and NH_4^+, suggesting a common anthropogenic origin. This correlation also depends on the secondary characteristic of these pollutants which are more dependent on meteorological conditions than on common anthropogenic sources, like atmospheric stability, wind speed and solar radiation.

The correlation between Na^+ and Cl^- indicated that they are mainly sea salt and the correlation among K^+, Ca^{2+} and Mg^{2+} indicated a crustal source as the main source. A higher correlation between Na^+ and Cl^- should be expected in this case, but the results shows that not necessarily all the Na+ comes from marine aerosol. Correlations between Mg^{2+} and Ca^{2+} with SO_4^{2-}, r = 0.837 and r = 0.831 respectively, indicate that these ions play an important role in the partial neutralization of atmospheric acidity.

Non-significant correlations were found among trace metals, with the exception of correlations between Fe-Cr and Cu-Cr.

3.3. Factor Analysis

To gain a better knowledge of the origin of heavy metals and inorganic ions in PM₁₀ particles, a statistical factor 6.4 analysis was applied. The results of the factor analysis of concentrations from 43 samples with 8 elements (V, Cr, Cu, Ni, Pb, Mn, Fe and Al) and from 131 samples with 8 ions (SO_4^{2-}, NO_3^-, Cl^-, NH_4^+, K^+, Na^+, Ca^{+2}, Mg^{+2}) are shown in Table **7**. Four factor groups explain 91.7% of the total variance. In the first factor, the ions NO_3^-, SO_4^{2-}, Na^+, NH_4^+ and the trace metals Cu, Cr and Fe were highly loaded. The ions NO_3^- and SO_4^{2-} are typical anthropogenic components generated by NO and SO_2 emitted by combustion sources and car exhaust. As Costa Rica has ocean coastline on both sides of the country, Na^+ is mainly ssalt (sea salt). The above trace metals indicated both crustal and anthropogenic sources, as Cr is emitted by electroplating processes. Potassium dichromate is widely used in industry as a fungicide in cooling towers, Fe is emitted by ferrous smelters, and Cu has many industrial applications in the manufacture of copper articles and electrical conductors, which produce Cu fumes.

This proves the fact of possible contribution of industrial emissions, located at North and Northeast of the city, to the composition of PM10. This factor accounted for 37.9% of total variance.

In the second factor, V and Pb, which are associated with anthropogenic emissions, were highly loaded. Vanadium in the form of vanadium oxide is a component in certain kinds

Table 4. **Trace Metal Average Concentrations Measured in PM₁₀ Particles Collected at Two Sites Located in the City of San Jose, from May 2007 to May 2008**

					Main Cathedral of San Jose				
Data	**PM₁₀ (µg/m³)**	**V (ng/m³)**	**Pb (ng/m³)**	**Cr (ng/m³)**	**Cu (ng/m³)**	**Ni (ng/m³)**	**Mn (ng/m³)**	**Al (ng/m³)**	**Fe (ng/m³)**
Mean	47.1	5.69	11.37	1.27	19.08	2.14	33.8	619.6	509.0
Max	110.0	17.21	72.18	5.99	47.78	3.97	88.7	1631	1369
Min	13.0	0.48	1.61	0.16	6.21	0.65	8.4	132.3	237.0
SD	16.8	5.0	14.2	1.4	8.2	0.8	20.1	455	242
					San Jose Board of Education Building				
Data	**PM₁₀ (µg/m³)**	**V (ng/m³)**	**Pb (ng/m³)**	**Cr (ng/m³)**	**Cu (ng/m³)**	**Ni (ng/m³)**	**Mn (ng/m³)**	**Al (ng/m³)**	**Fe (ng/m³)**
Mean	29.8	5.17	12.42	1.03	15.24	2.00	26.1	246.6	335.4
Max	49.0	20.8	46.1	3.4	38.9	4.3	63.0	787.7	466.5
Min	13.0	0.2	1.3	0.2	7.8	0.5	4.6	60.6	181.3
SD	6.7	5.5	12.1	0.9	6.2	1.0	15.5	155	72.1

Tabla 5.   Chemical Composition, Ions (µg/m^3) and Metals (ng/m^3) of PM$_{10}$ in Some Latin-American Cities

City	Date of Sampling	SO$_4^{2-}$	NO$_3^-$	Cl$^-$	NH$_4^+$	Na$^+$	Pb	Cr	Ni	V	Mn
Distrito Federal, México [8]	2003-2004	5.98	5.59	0.95	1.79	3.07	57.34	52.12	6.98	23.09	52.51
Buenos Aires, Argentina [20]	2002						70.56	2.83	1.70	3.53	21.23
Chillán, Chile [21]	2001-2003	4.15	8.60	0.32	4.78		22.45		6.41	18.50	38.54
Campinas, Brazil [22]	2003-2004						3.60	4.20	4.30	3.40	14.8
Guaiba, Brazil [23]	2001-2002							17.2	9.70	16.7	17.6
San José, Costa Rica (This study)	2007	3.02	0.20	0.61	0.39	0.76	11.90	1.15	2.07	5.43	29.95

Table 6.   Pearson´s Matrix Correlation Among the Results of Ions and Trace Metals Measured in PM10 Particles Collected at San Jose City, from May2007 to May 2008

	PM$_{10}$	Cl$^-$	NO$_3^-$	SO$_4^{2-}$	Na$^+$	NH$_4^+$	K$^+$	Mg^{2+}	Ca^{2+}	V	Pb	Cr	Cu	Ni	Mn	Al	Fe
PM$_{10}$	1.000																
Cl$^-$	0.107	1.000															
NO$_3^-$	**0.941**	0.429	1.000														
SO$_4^{2-}$	**0.894**	0.378	**0.924**	1.000													
Na$^+$	0.755	**0.773**	**0.905**	**0.846**	1.000												
NH$_4^+$	**0.774**	0.316	**0.784**	**0.857**	0.600	1.000											
K$^+$	0.587	0.590	0.723	0.494	**0.778**	0.649	1.000										
Mg^{2+}	0.714	0.047	0.658	**0.837**	0.435	0.635	0.019	1.000									
Ca^{2+}	**0.858**	-0.183	0.698	**0.831**	0.509	0.585	0.160	**0.827**	1.000								
V	0.428	0.096	0.407	0.357	0.594	-0.011	0.432	-0.073	0.399	1.000							
Pb	0.280	-0.485	0.122	0.012	0.045	-0.295	-0.095	-0.043	0.324	0.575	1.000						
Cr	**0.812**	0.497	**0.911**	**0.887**	**0.804**	0.733	0.514	0.752	0.624	0.173	0.059	1.000					
Cu	0.347	0.654	0.520	0.642	0.513	0.616	0.224	0.649	0.299	-0.229	-0.462	**0.793**	1.000				
Ni	-0.566	-0.210	-0.625	-0.558	-0.562	-0.173	-0.307	-0.446	-0.384	-0.265	-0.215	-0.495	-0.064	1.000			
Mn	-0.201	0.626	0.021	-0.159	0.127	0.281	0.484	-0.354	-0.533	-0.274	-0.483	0.131	0.386	0.415	1.000		
Al	0.492	0.549	0.656	0.393	0.656	0.466	**0.852**	0.037	0.013	0.206	-0.107	0.460	0.115	-0.641	0.328	1.000	
Fe	**0.886**	0.207	**0.898**	**0.846**	0.705	0.616	0.443	0.766	0.704	0.210	0.215	**0.845**	0.405	**-0.825**	-0.252	0.586	1.00

Bold numbers represent significant correlations at p<0.05. N=52.

of steel used in automobile parts, springs and ball bearings. It is also used in the manufacture of rubber, plastics, ceramic and other products [13]. This factor accounted for 14.7% of total variance.

In the third factor Cl$^-$, K$^+$, Mg^{2+} and Mn were highly loaded, and Na and Al moderately loaded. These ions and Al receive an important contribution from crustal material, although Mn also has anthropogenic origin. Significant Al and Mn, are emitted from single sources such as large smelters [14-16]. Al is also emitted by aluminumware manufacturing. Ni and Mn are mainly released from oil-fired furnaces and ferroalloys (Szefer and Szefer, 1986). This group accounts for 23.4% of total variance.

In the fourth factor, moderate loading was observed for Al and Fe, and high loading for Ni. As mentioned above, Al and Fe are mainly crustal. The total variance explained by this factor was 15.7%.

3.4. Enrichment Factors

To evaluate the contribution of anthropogenic sources, the enrichment factor EF$_c$ of an element was calculated using the following relationship:

$$EF_c = (Cx/CAl_{sample}) / (Cx/CAl_{crust}) \qquad (1)$$

where (Cx/CAl$_{sample}$) is the ratio of the concentration of element X to that of Al in the sample and (Cx/CAl$_{crust}$) is the corresponding ratio in crustal material [17].

Elements for which the earth's crust is the only source have an EF$_c$ of unity. Elements which have other sources than crustal material can be expected to have EF$_c$ greater than one.

Table **8** shows the EF$_c$ values calculated from the concentration of trace metals contained in PM$_{10}$ particles collected in the present study. Pb, Cu and V had the highest EF$_c$; 253.7,

Table 7. **Results from the Principal Component Analysis Normalized Varimax Applied to Chemical Species Contained in PM₁₀ Particles Collected in the City of San Jose**

| Components				
Groups	**PC 1**	**PC 2**	**PC 3**	**PC 4**
Cl^-	0.213	-0.185	**0.836**	0.123
NO_3^-	**0.774**	0.276	0.369	0.420
SO_4^{2-}	**0.918**	0.182	0.173	0.269
Na^+	**0.615**	0.374	**0.567**	0.332
NH_4^+	**0.774**	-0.090	0.401	0.056
K^+	0.247	0.313	**0.819**	0.288
Mg^{2+}	-0.258	-0.166	**0.931**	0.193
Ca^{2+}	**0.850**	0.375	-0.300	0.100
V	0.110	**0.939**	0.163	0.073
Pb	-0.037	**0.766**	-0.397	0.138
Cr	**0.856**	0.046	0.319	0.261
Cu	**0.752**	-0.425	0.372	-0.148
Ni	-0.296	-0.134	0.032	**0.927**
Mn	-0.134	-0.320	**0.839**	-0.293
Al	0.093	0.082	**0.657**	**0.714**
Fe	**0.722**	0.123	0.036	**0.661**
%Variance Explained	**37.9**	**14.7**	**23.4**	**15.7**

45.4 and 14.4 respectively. These values indicate anthropogenic sources such as emissions from industrial processes

and metalworking industries. The lowest EF_c values corresponded to Cr, Mn and Ni, showing that the principal contribution is from crustal material. EF_c values for Al and Fe indicated that they are crustal.

Table 8. **Enrichment Factors Calculated from the Trace Metal and Ion Concentrations Determined in PM₁₀ Particles Collected in the City of San Jose**

Metal	**EFc**
V	14.4
Pb	254
Cr	1.2
Cu	45.4
Ni	3.6
Mn	4.3
Fe	1.3

EF_c values were also calculated for inorganic ions, taking the sea aerosol as a reference, because Costa Rica is a narrow country, with an average width of 120 km and divided by a mountain range 3500 m above sea level. In the mornings the winds come from the Pacific Ocean but in the afternoon they come from the Caribbean Sea and blow through depressions in the mountain range. Na^+ was used as a reference to estimate EF_c, and sea water ion values were taken from Taylor and McLean (1985). Table **8** shows that Cl^- and Mg^{2+} are sea salts, while SO_4^{2-}, Ca^{2+} and K^+ receive contributions from other sources. The same conditions have been reported by Wu *et al*., (1994) [18] and Hernandez *et al*., (2006) [19].
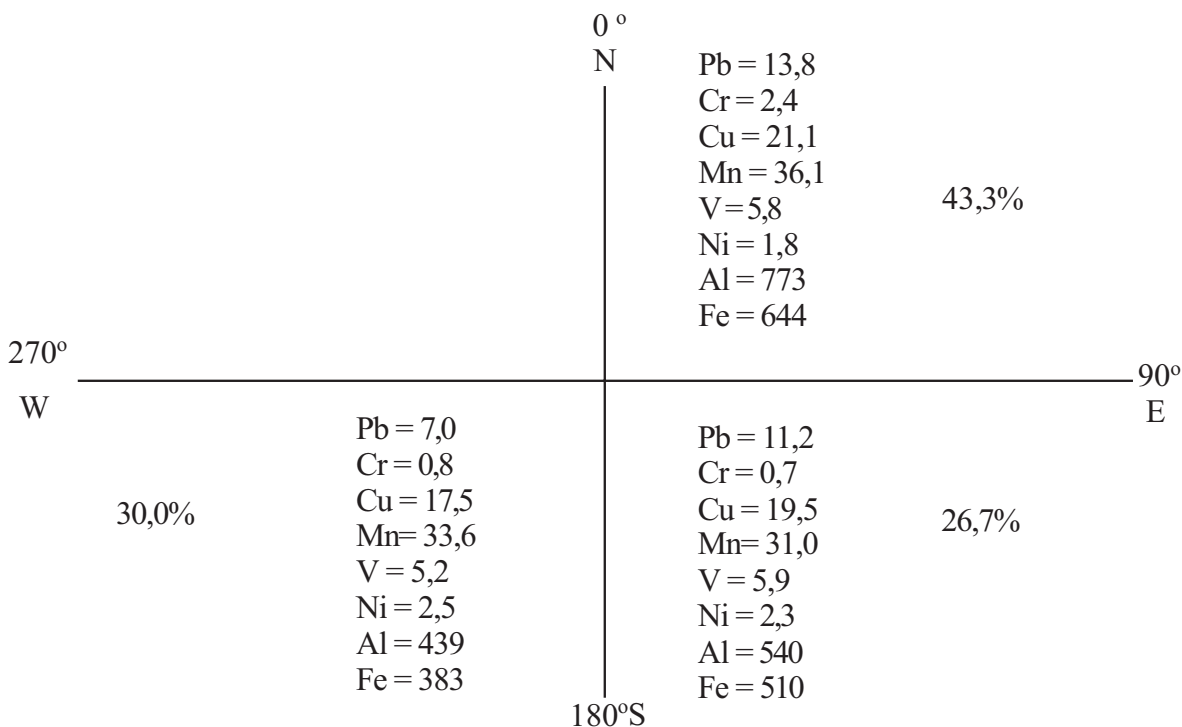
Fig. (2). Relation between concentrations of metals in PM₁₀ and wind trajectories for San José, City.

3.5. Effect of Wind Direction on Particle Composition

The Instituto Meteorológico de Costa Rica provided meteorological data collected at a weather station located 700m from the Aranjuez sampling site in the city of San Jose. These data allowed the effect of prevailing wind directions and speeds upon the chemical composition of PM_{10} aerosols to be evaluated. These trajectories were classified into four groups by quadrant (0 to 90°; 90° to 180° and so on). Fig. (**2**) shows the average trace metal concentrations by trajectory. It can be seen that the highest concentrations were in the first group (NE) for Pb, Cr, Al and Fe, while for the remaining metal concentrations they were not significantly different at the 5% probability level. This behavior can be explained by the influence of stationary source emissions from industrial areas located downwind toward the city.

4. CONCLUSIONS

The aim of this study is to contribute to a better understanding the origin of the trace metals V, Cr, Ni, Pb, Mn, and Fe, and of the inorganic ions Cl^-, SO_4^{2-} and NO_3^- contained in PM_{10} particles in the city of San Jose, Costa Rica. The results indicated that SO_4^{2-} had the highest concentration. It is considered ssalt, and there were also significant contributions from anthropogenic sources such as emissions from the combustion of diesel oil with high sulfur content of around 0.4%.

From the trace metal EF_c results, it was found that Pb, V and Cu receive a large contribution from the combustion of fossil fuels and metalworking industries located in the city of San Jose. Pb, Cr, Fe and Al concentrations are increased by the predominant N-NE winds that transport industrial and domestic emissions, which pass through the city where the sampling stations are located.

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REFERENCES

[1] Instituto Nacional de Estadística y Censos. Compendio de Estadísticas del Cantón Central de San José. Informe Técnico 2000.

[2] Herrera J, Rodríguez S. Cuarto Informe de Calidad del Aire de la ciudad de San José. Informe técnico. Universidad Nacional, Costa Rica 2007.

[3] Brunekreef B, Holgate ST. Air pollution and health—review. Lancet 2002; 360(9341): 1233-42.

[4] Lotufo PA, Bensenor IM. Asthma mortality in Brazil. Ann Allergy Asthma Immunol 1999; 83(6): 572-73.

[5] Benício MH, Cardoso MR, Gouveia NC, Monteiro CA. Secular trends in respiratory diseases of childhood in the city of Sao Paulo, Brazil (1984-1996). Revista de Saúde Pública 2002; 34(6): 91-101.

[6] Adamson IY, Prieditis H, Hedgecock C, Vincent R. Zinc is the toxic factor in the lung response to an atmospheric particulate sample. Toxicol Appl Pharmacol 2000; 166: 111-9

[7] Schwartz J, Meas LM. Fine particles are more strongly associated than coarse particles with acute respiratory health effects in schoolchildren. Epidemiology 2000; 11: 6-10.

[8] Báez AP, García RM, Torres BMC, *et al*. Origin of trace elements and inorganic ions in PM_{10} aerosols to the South of Mexico City. Atmos Res.2007; 85: 52-63.

[9] Bilos C, Colombo JC, Skorupka CN, Rodrigues PMJ. Sources, distribution and variability if airborne trace metals in La Plata City area, Argentina. Environ Pollut 2001; 111: 149-58.

[10] Braga CF, Teixeira EC, Meira L, Wieganda F, Yoneama ML, Dias JF. Elemental composition of PM_{10} and $PM_{2.5}$ in urban environment in South Brazil. Atmos Environ 2005; 39: 1801-15.

[11] Quintero SL, Sousa da Silva CR, Arbilla G, Escaleira V. Metals in airborne particulate matter in the industrial district of Santa Cruz, Rio de Janeiro, in an annual period. Atmos Environ 2004; 38: 321-31.

[12] IUPAC Recommendations. Pure Appl Chem 1995; 67: 1699-723.

[13] ATSDR (Agency for Toxic Substances and Disease Registry). ToxFAQs Vanadium and Compounds. US Department of Health and Human Services, Washington, DC. (CAS # 7440-62-2) 1995.

[14] Ross HB. The importance of reducing sample contamination in routine monitoring of trace metals in atmospheric precipitation. Atmos Environ 1986; 20: 401-5.

[15] Nriagu JO, Pacyna JM. Quantitative assessment of worldwide contamination of air, water and soils by trace metals. Nature1989; 333: 134-9.

[16] Szefer P, Szefer Z. Some metals and their possible sources in rain water of the southern Baltic Coast, 1976 and 1978-1980. Sci Total Environ 1986; 57: 79-89.

[17] Taylor SR, McLennan SM. The continental crust: its composition and evolution. Blackwell: Oxford, UK. 1985.

[18] Wu ZY, Han M, Lin ZC, Ondov JM. Chesapeake Bay atmospheric deposition study, year 1: sources and dry deposition of selected elements in aerosol particles. Atmos Environ 1994; 28: 1471-86.

[19] Hernández E, Gimeno L, Sánchez M, Rua A, Méndez R. Relationship between rain composition in Spain and its sources. J Geophys Res 1996; 101(D18): 23381-7.

[20] Smichowski P, Marrero J, Gomez D. Inductively coupled plasma optical emission spectrometric determination of trace element in PM10 airborne particulate matter collected in an industrial area of Argentina. Microchem J 2005; 80: 9- 17.

[21] Celis J, Morales J, Zaror C, Inzunza J. A study of the particulate matter PM10 composition in the atmosphere of Chillan, Chile. Chemosphere 2004; 54: 541-50.

[22] Miranda R, Tomaz E. Characterization of urban aerosol in Campinas, São Paulo, Brazil. Atmos Res 2008; 87: 147−57.

[23] Braga CF, Teixeira E, Meira L, Wiegand F, Yoneama ML, Dias JF. Elemental composition of PM_{10} and $PM_{2.5}$ in urban environment in South Brazil. Atmos Environ 2005; 39: 1801-15.