



Chemical characterization and source apportionment of PM₁₀ and PM_{2.5} in the metropolitan area of Costa Rica, Central America

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ABSTRACT

PM₁₀ and PM_{2.5} levels, concentrations of major ionic components, trace elements, and organic and elemental carbon were evaluated from samples collected in 4 sites (industrial, commercial and residential zones) located in the metropolitan area of Costa Rica. The annual mean PM levels were higher in high traffic–commercial (HE–01) and industrial (BE–02) sites, 55 µg m^{−3} and 52 µg m^{−3} for PM₁₀ and 37 µg m^{−3} and 36 µg m^{−3} for PM_{2.5}, respectively. The major components of PM_{2.5} were organic matter (OM) and elemental carbon (EC) (44.5–69.9%), and secondary ions (16.1–27.2%), whereas the major components of PM₁₀ were OM+EC (32.7–59.4%), crustal material (23.5–35.6%) and secondary ions (11.4–26.9%). For the most of the sampling sites, PM₁₀ and PM_{2.5} concentrations were lower during the dry season and increased gradually in the rainy season due to wind patterns. PMF model identified 8 principle sources for PM₁₀ and PM_{2.5} in the industrial site (crustal, secondary sulfate, secondary nitrate, secondary organic, traffic, sea–salt aerosols, industrial and oil combustion), 6 and 5 sources in commercial and residential sites, respectively. The source contributions showed a clear seasonal pattern for all the sites.

Keywords: PM₁₀, PM_{2.5}, chemical composition, Costa Rica, source apportionment

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1. Introduction

Atmospheric particulate matter (PM) is made up of solid and/or liquid particles (except pure water) of various sizes and compositions, including mineral dust, metals, metalloids, sea salts, ammonium nitrate and sulfate, organic compounds, elemental carbon, etc. The relative abundances of these atmospheric components in particulate matter are temporally and spatially highly variable. Some of them are directly emitted into the atmosphere by both natural and anthropogenic sources (primary particles), while some others are the result of homogeneous or heterogeneous nucleation and condensation of gaseous precursors (secondary particles) (Chan and Kwok, 2001; Morawska and Zhang, 2002). Secondary inorganic aerosols (SIA), i.e. ammonium sulfates and nitrates, are a result of these atmospheric reactions, being commonly observed in polluted air masses (Lammel and Leip, 2005). The PM can have different sources according to their size, for fine particles (particles with aerodynamic diameter ≤2.5 µm) they can be emitted primarily (such as diesel soot), or formed secondarily from gaseous precursors by nucleation and/or condensation on existing particles (Finlayson–Pitts and Pitts, 2000). The coarse fraction is also primarily emitted by mechanical processes (such as mineral dust and sea spray). Coarse secondary particles may also be found (Raes et al., 2000), due to chemical interaction of gases with primary particles of crustal or marine origin.

The growing interest aroused by atmospheric aerosols is due to their impact on human health, air quality and global climate change (WHO, 2006; Solomon et al., 2007; Colette et al., 2008). A large number of epidemiological studies show that aerosol particles, and in particular their fine fraction, pose a risk to human health because of their adverse effects both on the respiratory and cardiovascular systems (Pope and Dockery, 2006). Aerosol particles affect air quality with potentially negative effects on visibility, agricultural and natural ecosystems, material and cultural heritages (Gao et al., 2002; Lazaridis et al., 2002; Yadav and Rajamani, 2006; Yuan et al., 2006; Yatkin and Bayram, 2008). Atmospheric aerosols also influence the Earth's radiation balance both directly, by scattering and absorbing the in–coming and out–going radiations, and indirectly, by acting as cloud condensation nuclei (CCN) or ice nuclei (IN), thus changing the microphysical structure, the optical properties and the precipitation efficiency of clouds (Kaufman and Koren, 2006; Yu et al., 2006; Solomon et al., 2007). However, these sole mass level determinations make our understanding of the nature of several sources of contamination and the processes which affect the air quality rather incomplete. The careful analysis of the chemical composition is now considered of paramount importance in the chemistry of the urban atmosphere.

The metropolitan area of Costa Rica is located in a central plateau of around 3 000 km² surface including in a mountain system that cross the country from NW to SE, with mountains having a

maximum elevation of around 4 000 m. The metropolitan area is the highest-ranking center in the urban system in Costa Rica, accounting for 75% of the vehicle fleet (approximately 734 200 units), 65% of the domestic industry and 60% of the country's population (2 580 000), according to data from the last population census conducted in 2010 (INEC, 2011). Lack of urban planning has implicated a considerable ruin of air quality, as a result of growth experienced by the cities of the metropolitan area of Costa Rica during the past 20 years.

This paper focuses on the much-needed information on particulate matter chemical composition and their sources of formation, as well as their spatial and seasonal characteristics in urban and semi-urban areas of the metropolitan area of Costa Rica. This comprehensive dataset will be a key tool to policy makers in providing vital information for designing effective particulate matter control strategies.

2. Experimental

2.1. Sampling

For the PM₁₀ and PM_{2.5} sampling, four monitoring sites were selected (Figure 1). The sites were representative of commercial, industrial and residential areas, all located in the Costa Rica metropolitan area (Table 1). Sampling campaign was conducted between June 2010 and July 2011. Simultaneous samples were collected once every six days. To collect PM₁₀ samples, four high volume air samplers, Thermo Andersen with MFC (Mass Flow Controller) were used with a flow rate of $(1.13 \pm 10\%) \text{ m}^3 \text{ min}^{-1}$. Flow calibration of each sampler was performed comparing the readings of pressure drop generated by the flow passing through a calibrated critical orifice (TISCH VARIFLO Model 454) with the sampler pressure drop reading.

For PM_{2.5} sampling, four low volume air samplers (Air Metrics) were used with a flow rate of 5 liters per minute. The separation of the PM_{2.5} fraction was done at the entrance of the sample by a head with two impactors, one (located on the top) that separates the total PM₁₀ and a second impactor that separates the fraction of PM_{2.5} particles of the PM₁₀.

Samples were taken during 24 h on pre-fired (at least 5 h at 900 °C) pre-conditioned (24 h in a dessicator under the following conditions: temperature of 15–30 °C and humidity less than 40%) and pre-weighted quartz fiber filters (Whatman CAT No. 1851–865 and Pallflex TYPE: Tissuquartz 2500 QAT-UP for PM₁₀ and PM_{2.5}, respectively). Before and after collection, the samples were stored in the freezer and they were also kept frozen during transport. After particle collection, the filters were reconditioned for another 24 h in an air conditioned room and subsequently analyzed for total mass. After re-weighing, the exposed filters were stored in a freezer at –5 °C to limit losses of volatile components.

All procedures during handling of filters were strictly quality controlled to avoid any possible contamination.

2.2. Chemical analysis

Samples collected in quartz filters were used for gravimetric analysis in order to determine the PM₁₀/PM_{2.5} concentrations. The weighing of the low volume filters was performed using a semi-microanalytic balance (Mettler). The readability of the balance is 10 µg with a precision of $\pm 40 \text{ µg}$ corresponding to mass concentration uncertainty of $\pm 0.86 \text{ µg m}^{-3}$ for PM_{2.5} samples. High volume filters used in PM₁₀ collection were weighted in an analytical balance. The mass concentration uncertainty of PM₁₀ samples was $\pm 1.22 \text{ µg m}^{-3}$.

Table 1. Description of sampling sites

Site	Sampling Site Type	Municipality	Location
SJ-03	Commercial	San Jose	National Electrical Company (CNFL) Office
HE-01	High Traffic-Commercial	Heredia	National University Central Administration Building
BE-02	Industrial	Belen	Intermodal Company Office
MO-01	Residential	Moravia	EATON Company Office

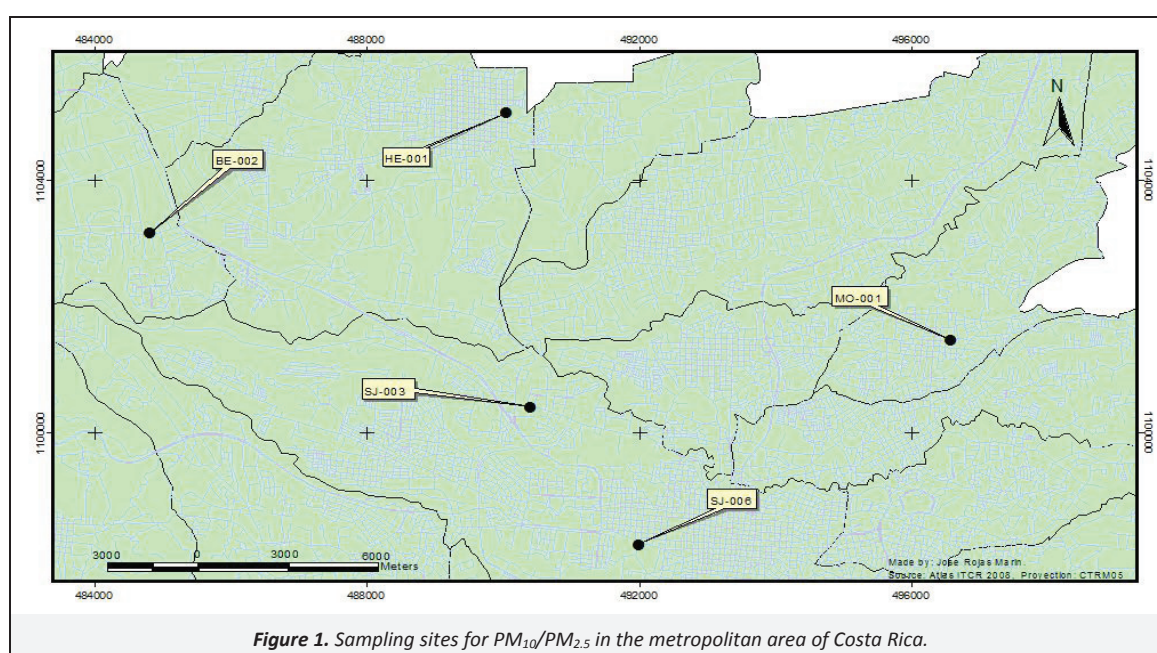


Figure 1. Sampling sites for PM₁₀/PM_{2.5} in the metropolitan area of Costa Rica.

A small portion of quartz filters were analyzed for organic carbon (OC) and elemental carbon (EC) using DRI Model 2001 Thermal/Optical Carbon Analyzer (Atmoslytic Inc., Calabasas, CA, USA). A 0.68 cm² punch from each filter was analyzed for eight carbon fractions following the IMPROVE TOR protocol. This produced four OC fractions (OC1, OC2, OC3, and OC4 at 120, 250, 450, and 550 °C, respectively, in a helium atmosphere), a pyrolyzed carbon fraction (OP, determined when reflected laser light attained its original intensity after oxygen was added to the combustion atmosphere), and three EC fractions (EC1, EC2, and EC3 at 550, 700, and 800 °C, respectively, in a 2% oxygen and 98% helium atmosphere). IMPROVE OC is operationally defined as OC1+OC2+OC3+OC4+OP and EC is defined as EC1+EC2+EC3–OP. For the OC and EC determination, the analyzer was calibrated using different aliquots (0, 3, 5, 7, 10, 12, 15, 20 and 25 µl) of a standard sucrose solution (4 260 mg L⁻¹) over a filter blank (pre-heated quartz filter punch). The limits of detection (LODs) for OC and EC were 746 ng m⁻³ and 180 ng m⁻³, respectively. Analytical uncertainties for OC and EC were estimated to be 16% and 9%, respectively. NIST 8785 reference material was used in order to evaluate the analytical method accuracy for the determination of organic and elemental carbon in PM₁₀/PM_{2.5}. This reference material consists of a thin fraction of SRM 1649 (Urban Dust) deposited on a quartz fiber filter. Seven replicates of NIST 8785 were analyzed. An overall bias between –3.7 and 5% was obtained. There was no significant difference between the means of the obtained values and the reference values, according to a t-test with a 95% confidence level.

Another filter portion was extracted in 50 mL deionized water during 35 minutes in an ultrasonic bath. The analysis of ionic species was performed by dual microbore suppressed Ion Chromatography using a DIONEX ICS–3000 equipment with a quaternary pump. A fresh calibration curve was prepared for every 20 samples, together with a dissolution of quality control of 5 mg L⁻¹ prepared from a certified DIONEX synthetic sample. Detection limits for each ion are shown in Table 2.

Table 2. Limit of detection (LOD) for different chemical species analyzed in PM_{2.5} and PM₁₀

Chemical Specie	LOD	Chemical Specie	LOD
Metals (ng m ⁻³)		Inorganic Ions (µg m ⁻³)	
Na	125	F ⁻	0.01
K	57	Cl ⁻	0.05
Ca	34	Br ⁻	0.02
Mg	17	NO ₂ ⁻	0.02
Cu	0.78	NO ₃ ⁻	0.01
Fe	0.54	PO ₄ ³⁻	0.06
Mn	0.43	SO ₄ ²⁻	0.03
Al	0.88	NH ₄ ⁺	0.01
Cr	0.97		
Ni	0.51		
V	0.14		
Pb	0.35		

Other filter portion was extracted by adding 5 mL of ultra-pure concentrated nitric acid and 25 mL of deionized water and heated on a hot plate until almost dryness. The remaining solution was poured into a 25 mL volumetric flask. A second extraction was done with 1 mL of concentrated HClO₄. Analyses of metals were made using atomic absorption spectrometry (PERKIN ELMER AANALYST 700) with a graphite furnace. Detection limits in ng m⁻³, using the IUPAC method, were obtained. The results are shown in Table 2. Blank filters were analyzed for metals and inorganic ions, obtaining lower concentrations of 5% of those found in samples. The accuracy of the metal chemical analysis was periodically checked using a certified standard (SRM 1648) spiked on blank

filters. An overall bias between –8 and 13% was obtained for metal concentrations measured in samples.

Finally, contents of Si and CO₃²⁻ were determined indirectly from the contents of Al, Ca and Mg, on the basis of prior experimental equations (1.89 Al = Al₂O₃, 3 Al₂O₃ = SiO₂; 1.5 Ca + 2.5 Mg = CO₃²⁻) (Marcazzan et al., 2001).

2.3. Positive matrix factorization (PMF)

The PMF model was used here to identify PM₁₀ and PM_{2.5} sources and estimate source contributions. It is a multivariate receptor model that has been described in detail by Paatero (1997) and implemented in the PMF2 program, which doesn't require source profile knowledge unlike traditional source receptor models like Chemical Mass Balance (CMB). This program is now being widely used to analyze airborne particulate matter sources (Kim et al., 2003; Hien et al., 2004; Mazzei et al., 2008).

PMF is a receptor model based on the principle that a relationship between sources and receptor exists when mass conservation can be assumed (Paatero and Hopke, 2003). In this case, and when chemical speciation of ambient PM is available, a mass balance equation of the following form can be written:

$$x_{ij} = \sum_{h=1}^p g_{ih} f_{hj} + e_{ij} \quad (1)$$

where x_{ij} is the j^{th} species concentration measured in i^{th} sample, g_{ih} is the particulate mass concentration from the h^{th} source contributing to the i^{th} sample, f_{hj} is the j^{th} species concentration measured in the i^{th} sample, and p is the total number of independent sources. The corresponding matrix equation is:

$$X = GF + E \quad (2)$$

where X is a $n \times m$ matrix with n measurements and m elements. E is an $n \times m$ matrix of residuals. G is $n \times p$ source contribution matrix with p sources, and F is a $p \times m$ source profile matrix.

The signal-to-noise ratio (SNR) was used to select the species for further analysis. This ratio is defined as:

$$\left(\frac{S}{N}\right)_j = \sqrt{\frac{\sum_{i=1}^n (x_{ij} - s_{ij})^2}{\sum_{i=1}^n s_{ij}^2}} \quad (3)$$

Species with S/N below 0.2 were classified as bad values and were thus excluded from further analysis. The application of PMF depends on the estimated uncertainties for each of the data values. The uncertainty estimation provides a useful tool to decrease the weight of missing and below detection limit data in the solution. The procedure of Polissar et al. (2001) was used to assign measured data and the associated uncertainties as the input data to the PMF. The concentration values were used for the measured data, and the sum of the analytical uncertainty and 1/3 of the detection limit value was used as the overall uncertainty assigned to each measured value. Values below the detection limit were replaced by half of the detection limit values and their overall uncertainties were set at 5/6 of the detection limit values. Missing values were replaced by the geometric mean of the measured values and their accompanying uncertainties were set at four times of this geometric mean value. In addition, the estimated uncertainties of species that have scaled residuals larger than 72 need to be increased to reduce their weight in the solution (Paatero, 2000; Hopke and Paatero, 2002).

3. Results and Discussion

3.1. PM levels and chemical composition

Table 3 shows a statistical analysis of the PM component levels. The annual mean PM levels were higher in high traffic commercial (HE-01) and industrial (BE-02) sites, $55 \mu\text{g m}^{-3}$ and $52 \mu\text{g m}^{-3}$ for PM_{10} and $37 \mu\text{g m}^{-3}$ and $36 \mu\text{g m}^{-3}$ for $\text{PM}_{2.5}$, respectively. These two sites showed values that exceeded the Costa Rican Air Quality Annual Standard of $50 \mu\text{g m}^{-3}$ for PM_{10} . Residential site showed the lower values, $25 \mu\text{g m}^{-3}$ and $18 \mu\text{g m}^{-3}$, for PM_{10} and $\text{PM}_{2.5}$ respectively. It was found that the $\text{PM}_{2.5}$ concentration in all the sampling sites was higher than $15 \mu\text{g m}^{-3}$, which is the annual goal of the USA National Ambient Air Quality Standard. Daily concentrations exhibited 34% and 26% exceedances of the 24 h limit of the USA $\text{PM}_{2.5}$ National Ambient Air Quality Standard ($35 \mu\text{g m}^{-3}$) at the high traffic commercial (HE-01) and the industrial site (BE-02), respectively; indicating the necessity for local authorities to implement appropriate measures for PM emissions reduction. The comparison was done with USA standards as Costa Rica doesn't have an air quality standard for $\text{PM}_{2.5}$.

The two fractions of particulate matter are well correlated over the whole campaign, especially in the residential site ($R^2=0.85$). Lower correlation coefficients were obtained in commercial ($R^2=0.76$) and industrial ($R^2=0.70$) sites, probably, due

to the contribution of high levels of coarse particles generated by local industrial activities. The $\text{PM}_{2.5}/\text{PM}_{10}$ ratio values were 0.70, 0.72, 0.67 and 0.65 for SJ-03, MO-01, HE-01 and BE-02, respectively. More than 90% of sulfate particles are fine. Additionally, trace elements like V and Ni, have a predominantly fine granulometry especially in commercial and industrial sampling sites as these metals are emitted mostly by anthropogenic activities such as traffic, industrial combustion, etc. Values lower than 0.50 were obtained in the Al, Ca and other major components associated with crustal material.

An aerosol mass reconstruction (AMR) analysis was conducted to explore the relative contributions of the measured inorganic and organic chemical species and their relationship to the total measured gravimetric mass. For the purpose of chemical mass reconstruction, chemical components were grouped into six categories: crustal materials (CM), trace elements (TE), organic matter (OM), elemental carbon (EC), sea salt (SS), and secondary ions (SI). CM represents the sum of typical crustal materials, including Al, K, Fe, Ca, Mg, Ti and Si. Each of these species were multiplied by the appropriate factors to account for their common oxides based on the following equation (Marcazzan et al., 2001; Hueglin et al., 2005):

$$\text{CM} = 1.89 \text{ Al} + 1.21 \text{ K} + 1.40 \text{ Ca} + 1.66 \text{ Mg} + 2.14 \text{ Si} + 1.43 \text{ Fe} \quad (4)$$

Table 3. Annual average PM_{10} and $\text{PM}_{2.5}$ levels and their chemical compositions at the metropolitan area of Costa Rica

	SJ-03		MO-01		HE-01		BE-02	
	PM_{10}	$\text{PM}_{2.5}$	PM_{10}	$\text{PM}_{2.5}$	PM_{10}	$\text{PM}_{2.5}$	PM_{10}	$\text{PM}_{2.5}$
N	67	64	55	61	64	59	58	62
Inorganic Ions ($\mu\text{g m}^{-3}$)								
PM	37±9	26±7	25±7	18±5	55±15	37±12	52±18	36±15
F ⁻	0.08±0.07	0.04±0.06	0.08±0.04	0.05±0.03	0.08±0.02	0.06±0.03	0.07±0.03	0.08±0.02
Cl ⁻	1.17±0.86	0.52±0.51	1.08±0.65	0.51±0.47	0.98±0.60	0.46±0.42	1.01±0.62	0.57±0.77
NO ₂ ⁻	0.20±0.06	0.15±0.04	0.20±0.03	0.14±0.05	0.27±0.08	0.18±0.06	0.21±0.05	0.14±0.04
NO ₃ ⁻	0.86±0.34	0.63±0.15	0.92±0.32	0.58±0.27	1.13±0.41	0.74±0.39	1.02±0.36	0.60±0.29
PO ₄ ³⁻	0.67±0.55	0.31±0.28	0.71±0.57	0.24±0.34	0.54±0.17	0.40±0.15	0.41±0.17	0.53±0.12
SO ₄ ²⁻	3.23±1.68	3.34±1.23	3.45±2.17	3.15±1.66	3.87±1.65	3.52±1.38	3.97±1.80	3.81±1.62
NH ₄ ⁺	1.51±0.84	1.59±0.57	1.34±0.81	1.46±0.49	1.62±0.74	1.71±0.61	1.48±0.73	1.55±0.47
OC	6.67±2.85	6.73±2.17	4.27±2.56	4.45±2.37	14.67±8.44	13.86±6.57	13.34±4.92	12.55±5.12
EC	4.23±2.38	4.5±2.24	1.36±0.70	1.37±0.85	4.82±1.42	3.74±1.25	3.81±1.69	3.55±1.83
Metals (ng m ⁻³)								
V	3.7±1.6	2.9±1.1	1.2±0.6	0.9±0.7	2.8±1.2	2.1±0.9	5.4±3.6	3.6±2.4
Pb	11.8±5.3	7.6±3.7	8.6±3.0	7.29±2.17	11.5±3.9	8.75±1.77	11.2±6.8	9.9±4.7
Cr	11.5±4.5	7.0±2.6	5.7±1.6	5.1±1.9	4.9±1.3	6.7±1.1	8.7±4.4	7.9±2.5
Cu	47±28	43±20	86±38	57±41	84±54	62±43	146±65	96±51
Ni	4.6±1.4	3.86±0.95	3.4±2.3	2.94±1.81	2.1±0.8	1.74±0.55	7.0±3.6	5.9±2.4
Mn	58±32	61±29	84±39	44±17	139±71	67±36	136±24	58±17
Al	670±106	259±174	575±117	278±71	757±87	274±61	742±277	353±191
Fe	361±150	257±162	189±58	141±25	431±203	191±85	553±247	212±108
Ca	283±76	208±83	351±74	184±68	279±107	152±90	367±223	232±175
Mg	139±48	47±28	112±42	41±27	102±52	37±29	154±68	55±44
Na	1 440±425	615±317	1 291±805	554±392	1 306±567	677±357	1 394±376	665±228
K	236±104	125±91	123±39	81±45	124±45	65±32	231±102	117±81
Si	3 798±402	1 467±375	3 260±298	1 577±387	4 295±411	1 554±543	4 208±627	2 002±492

The Ca and Mg oxides were calculated using the non-sea salt (nss) portion of Ca and Mg. OM was obtained by multiplying the measured concentration of organic carbon (OC) by a factor of 1.6, which is based on an average of the recommended ratios of 1.6 ± 0.2 for urban aerosols and 2.1 ± 0.2 for aged or non-urban aerosols (Turpin and Lim, 2001). This factor is commonly used to estimate the unmeasured hydrogen and oxygen in organic compounds. The sea salt contribution represents particles in the form of fresh sea salt. It is calculated as the sum of measured chloride ion concentration plus the sea salt fraction of concentrations of Na^+ , Mg^{2+} , K^+ , Ca^{2+} , SO_4^{2-} based on the composition of seawater and ignoring atmospheric transformations (Seinfeld and Pandis, 2006):

$$\text{SS} = \text{Cl}^- + \text{ssNa}^+ + \text{ssMg}^{2+} + \text{ssK}^+ + \text{ssCa}^{2+} + \text{ssSO}_4^{2-} \quad (5)$$

where $\text{ssNa}^+ = 0.556 \text{ Cl}^-$, $\text{ssMg}^{2+} = 0.12 \text{ ssNa}^+$, $\text{ssK}^+ = 0.036 \text{ ssNa}^+$, $\text{ssCa}^{2+} = 0.038 \text{ ssNa}^+$, and $\text{ssSO}_4^{2-} = 0.252 \text{ ssNa}^+$ (Terzi et al., 2010). The EC contribution was reported as measured by thermal optical reflectance (TOR). The SI contribution was calculated as the sum of nss-SO_4^{2-} , NH_4^+ , and NO_3^- , where nss-SO_4^{2-} is total measured SO_4^{2-} minus the sea salt fraction of SO_4^{2-} . Trace elements were also converted to their common oxides. Trace elements only represent a small percentage of the total PM mass, however they were also added to the analysis because they have a great environmental importance due to their toxicity and anthropogenic origin. TE contribution was calculated using the following equation (Marcazzan et al., 2001):

$$\text{TE} = 1.47 \text{ V} + 1.29 \text{ Mn} + 1.27 \text{ Ni} + 1.25 \text{ Cu} + 1.08 \text{ Pb} + 1.31 \text{ Cr} \quad (6)$$

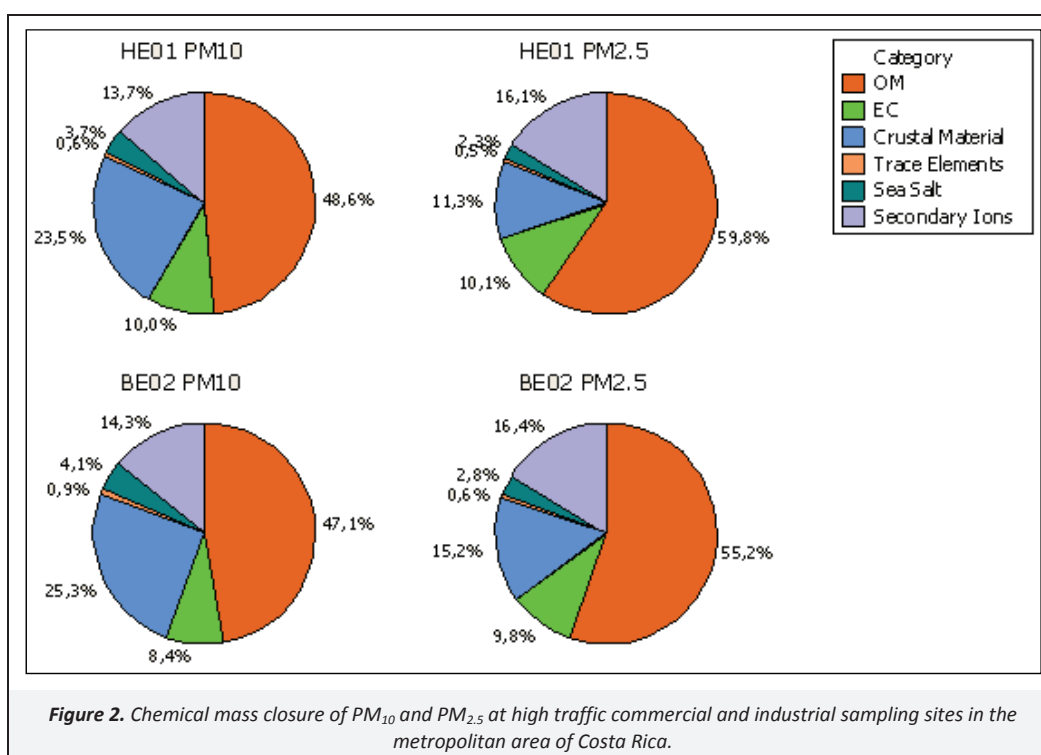
The coefficients in Equation (6) represent a gravimetric factor to obtain the corresponding oxides. The gravimetric and reconstructed mass concentrations show a generally strong correlation, with a coefficient of determination (R^2) range between 0.65–0.74, indicating overall good agreement between the reconstructed mass and the gravimetric mass. The major components of PM_{10} (Figure 2) in the four sampling sites were organic matter (OM) (27.3–48.6%), elemental carbon (EC) (5.4–12.8%) and crustal material (23.5–35.6%). The major components of $\text{PM}_{2.5}$ were

OM+EC (44.5–69.9%), and secondary ions (16.1–27.2%). The crustal contribution to $\text{PM}_{2.5}$ mass increased from 23–25% in industrial and commercial areas to 36% in residential areas which can be due to the presence of nearby non-urban lands, since these regions are subjected to wind resuspension (or entrainment) processes. The resuspension of dust (crustal materials of diameter $< 20 \mu\text{m}$) by wind provides a potential source of particles to the atmosphere (Loosmore and Hunt, 2000).

The contribution of marine aerosol varies between 4 to 7% for sampling sites presenting a fairly regular basis. This evidences that the contribution of this component is due to a regional scale phenomena. The levels of organic matter and elemental carbon (OM+EC) are higher in HE-01 and BE-02 and representing between 65 and 69% of the total mass of particles $\text{PM}_{2.5}$. These results show the importance of the contribution of combustion processes to the composition of fine particles. The trace metals represent the smallest contribution for all monitoring sites.

3.2. Temporal variations in PM_{10} and $\text{PM}_{2.5}$ chemical composition

Two different behaviors were found in the time series analysis for PM_{10} and $\text{PM}_{2.5}$ in the Metropolitan Area of Costa Rica. For MO-01, HE-01 and SJ-03, PM_{10} and $\text{PM}_{2.5}$ concentrations were lower during the dry season (January–April) and increased gradually in the rainy season (Figure 3). This situation can be explained as during the dry season, the average wind speed in the Metropolitan Area increases as a result of the influence of Alisios winds movement from the Caribbean Sea favoring the dispersion of pollutants. During the rainy season, Alisios winds reduce their intensity and allow the entry of Pacific breezes (generating rains in the zone) reducing the wind speed by 35%. This situation decreases the pollutant dispersion in the metropolitan area. For BE-02, higher concentrations were reported in dry season since this sampling point is located in the wind exit of the metropolitan area. As a result of this situation if pollutant dispersion decreases in the metropolitan area, the concentrations of particulate matter would be enhanced in BE-02. This explanation is in accordance with the correlation coefficient observed between HE-01 and BE-02 ($r = -0.768$).



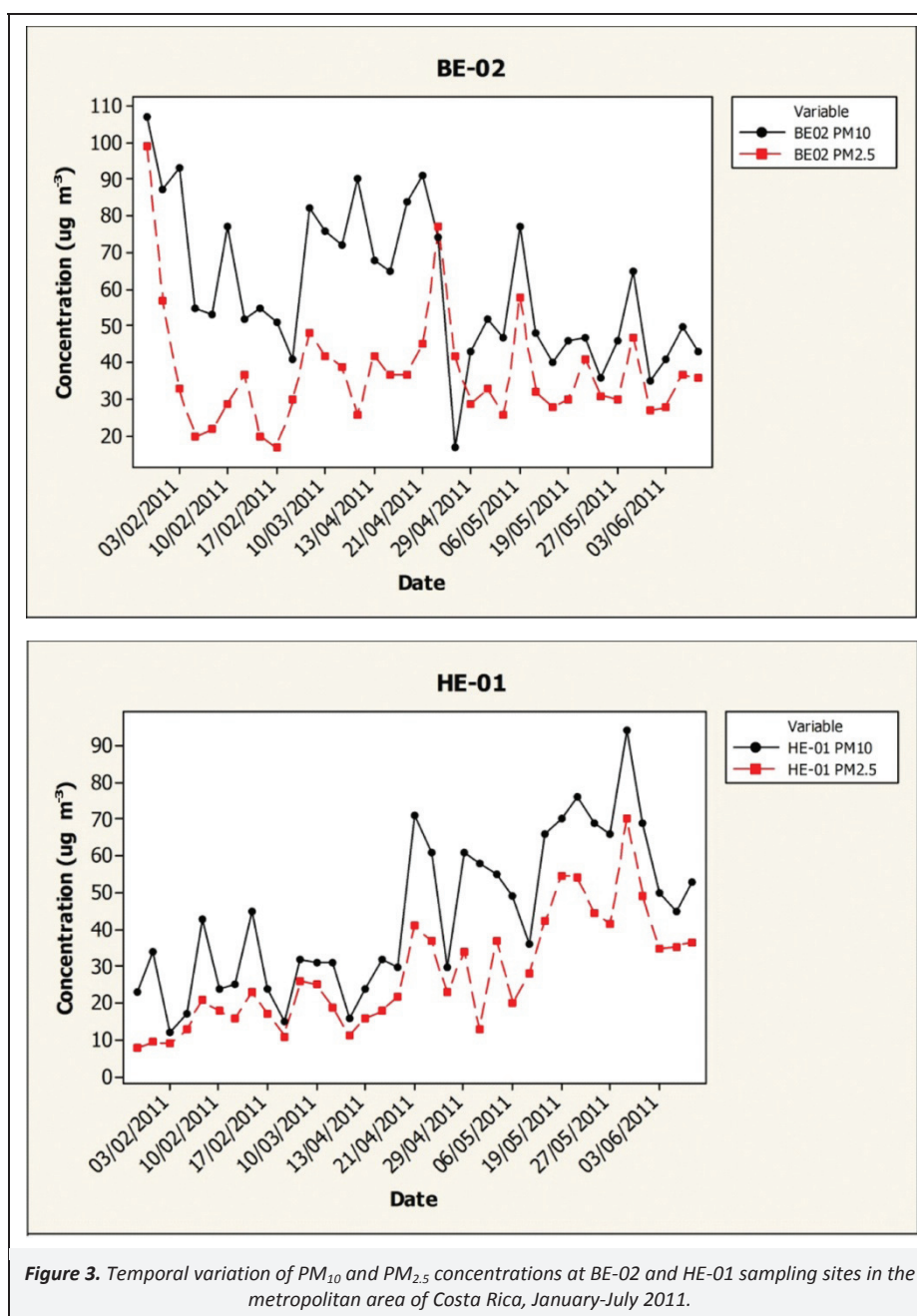


Figure 3. Temporal variation of PM_{10} and $PM_{2.5}$ concentrations at BE-02 and HE-01 sampling sites in the metropolitan area of Costa Rica, January–July 2011.

Figure 4 shows the temporal variation of major components in PM_{10} and $PM_{2.5}$ for SJ-03 sampling site. Because the variations were similar to the other sites, the results for these sampling stations are not plotted. Carbonaceous particle concentration (organic matter and elemental carbon), both coarse and fine fractions showed a clear seasonal pattern. The OC and EC in PM_{10} have showed lower concentrations in dry season (December–April) and higher values in rainy season (May–November). By comparing the results for dry and rainy seasons, at the same sampling sites, it is evident that the average OC and EC concentrations for $PM_{2.5}$ and PM_{10} during the rainy season were around 1.3–2.4 times higher than dry season. This can be explained by a reduction in the pollution dispersion in the metropolitan area of Costa Rica in rainy season. In the same way, temperatures during rainy season are lower than dry season helping the condensation process that produces secondary organic aerosols.

The crustal matter and sea salt concentrations presented their highest values in dry season due to the influence of Alisios winds that have speeds around 30 km h^{-1} favoring the movement of air mass from Caribbean Sea. The occurrence of high speed winds can

increase the contribution of resuspension process to the chemical composition of particles.

Sulfate concentrations showed a clear seasonal trend. The mean concentrations in dry season were slightly higher than in rainy season because of the stronger solar radiation in dry season, which promotes the oxidation of SO_2 to SO_4^{2-} . On the other hand, nitrate levels were characterized by a clear maximum in rainy season and a minimum in dry season, both for PM_{10} and $PM_{2.5}$ fractions. However, sulfates showed the opposite pattern. This is probably due to the low thermal stability of NH_4NO_3 in dry season when, under warm conditions, the formation of gaseous HNO_3 is favored. The concentration of sulfate in coarse and fine fraction was similar, which indicated that SO_4^{2-} was mostly present as ammonium sulfate (Harrison et al., 2003). In the case of nitrate, the ratio $PM_{2.5}/PM_{10}$ was not as high as expected, may be due to the presence of NaNO_3 and $\text{Ca}(\text{NO}_3)_2$ in the coarse fraction (Yin and Harrison, 2008). Ammonium levels at PM_{10} exhibited a clear minimum in dry season and the fine fraction showed no seasonal variation.

3.3. Organic and elemental carbon

The origin of OC and EC can be evaluated by the relationship between OC and EC (Turpin and Huntzicker, 1995; Chow et al., 1996). OC–EC strong correlations (r) of 0.64–0.77 and 0.78–0.88 were observed for PM_{10} and $PM_{2.5}$ respectively, in all the sampling sites. These correlations indicated the presence of common dominant sources for OC and EC (e.g. industrial combustion, motor vehicle exhaust) because the relative rates of EC and OC emissions would be proportional to each other. OC and EC had their strongest correlation in rainy season (0.78–0.84) implying that the majority of OC was primary and secondary organic compounds (SOC) formation might be minor. Lower values during dry season (0.69–0.72) can be due to a possible contribution of particles produced by resuspension process and the variations in SOC formation. The SOC is estimated by means of the following equation (Chow et al., 1996):

$$OC_{sec} = OC_{tot} - EC \left(\frac{OC}{EC} \right)_{prim} \quad (7)$$

where OC_{sec} is the secondary OC, and OC_{tot} is the measured total OC. The primary organic carbon (POC) could be calculated from the formula $EC(OC/EC)_{prim}$. However, the primary ratio of OC/EC is usually not available because it is affected by many factors such as the type of emission source as well as its variation in temporal and spatial scales, ambient temperature, and carbon determination method, etc. In many cases, $(OC/EC)_{prim}$ was represented by the observed minimum ratio $[(OC/EC)_{min}]$, and assumptions regarding the use of this procedure were discussed in detail by Castro et al. (1999).

The annual average concentrations of estimated SOC in the metropolitan area of Costa Rica contribute with 48% and 56% of the OC in PM_{10} and $PM_{2.5}$, respectively. Compared with rainy season results, there is an overall trend towards lower SOC levels but with a higher percentage of SOC in the TOC at each site during the dry season. Higher temperatures and more intense solar radiation during the dry season summer months provide favorable conditions for photochemical activity and SOC production.

3.4. Sources contribution

The sampling sites for PM_{10} and $PM_{2.5}$ were divided into three categories (industrial, commercial and residential) in the PMF analysis. The respective error estimates of masses, OC, EC, ionic compounds and elements were computed, and incorporated in the PMF model which was applied for each category separately.

For the industrial sampling site (BE–02), eight sources were identified as a result of PMF analysis. However, in commercial sites (SJ–03 and HE–01), six sources including: secondary sulfate, secondary nitrate, secondary organic, crustal, traffic and sea salt were identified successfully. A good correlation ($r=0.837$ and 0.852 for PM_{10} and $PM_{2.5}$, respectively) was obtained between predicted versus measured PM_{10} mass concentration showed that the model adequately reproduced the observed mass. In the residential zone sampling site (MO–01), only five sources were successfully identified: crustal, sea salt, traffic, secondary sulfate and secondary nitrate.

The first source in Table 4 was identified as vehicle exhaust based upon the abundances of EC, OC, SO_4^{2-} and certain amount of Fe. Both diesel and gasoline powered vehicles generate large amounts of carbonaceous compounds but the ratios of OC to EC in the emission profile can be quite different. Watson et al. (1994) noted that the OC/EC mass concentration ratio was 2.2 for gasoline fueled vehicle exhaust, 1.2 for diesel-fueled vehicle exhaust, and 1.1 for a mixture of vehicle types in roadside test. The common source attributed to these metals is resuspension of road dust due to traffic activity, mainly wear and tear of tires, brake wear and oil burning (Kulshrestha et al., 2009). The mean contributions to PM_{10} and $PM_{2.5}$ by traffic at residential site (MO–01), were calculated to be 7.1 and $4.7 \mu g m^{-3}$ respectively and at high traffic commercial site (HE–01) these were estimated to be 10.2 and $5.1 \mu g m^{-3}$. Lower contribution of vehicle exhaust was obtained for the industrial site (BE–02) (Table 5).

The second source identified by PMF was distinguished by large contribution values for Ni and V, which are good indicators for residual oil combustion (Chow and Watson, 2002). The contribution of these sources represents 7.5 and 11.8% of the PM_{10} and $PM_{2.5}$ mass concentration at BE–02.

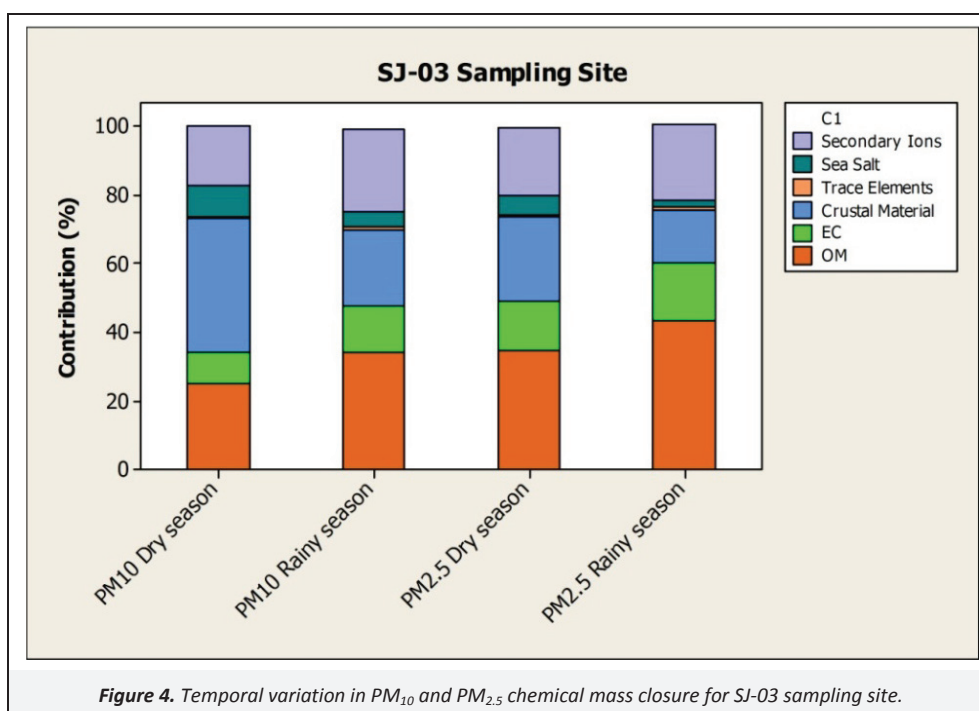


Table 4. Profiles of particulate sources resolved by PMF analysis for the industrial site BE-02. Values listed here correspond to mass percentage of each component

Sources	Vehicle Emission	Residual Oil	Sea Salt	Crustal Material	Secondary Organics	Secondary Sulfate	Secondary Nitrate	Industrial
PM _{2.5}								
SO ₄ ²⁻	2.91	15.11	0.94	10.39	12.72	60.2	1.37	0.38
NO ₃ ⁻	0.09	0.22	0.55	9.22	0	0.11	33.1	0.27
NH ₄ ⁺	0	0.93	0	0.77	0	15.33	8.17	0.11
OC	53.9	28.84	0	0.12	83.45	16.28	48.5	42.7
EC	39.7	43.92	0.86	1.18	0	7.15	5.11	9.2
V	0.28	2.07	0	0	0	0.05	0.1	9.9
Pb	0.05	0.33	0	0	0.33	0	0.04	20.5
Ni	0	2.39	0	0	0	0	0	0
Na	0	0.01	34.1	1.25	0	0.03	0	0
Cl	0.03	0	55.27	0	0	0	1.07	0
Mn	0.05	0	0.05	3.79	0	0	0	0
Al	0	0.02	0.01	12.56	0.87	0	0	0
Ca	0.17	0	3.11	21.77	1.09	0	0.97	0
Mg	0	0	2.96	15.02	0	0.02	1.16	0
K	0	2.85	1.08	8.17	0	0.12	0	0
Fe	1.55	0.03	0	16.43	0.87	0.07	0	7.3
Cu	0	0.07	0	0.11	0	0.14	0	14.10
PM ₁₀								
SO ₄ ²⁻	3.04	14.73	1.1	5.53	11.85	51.4	2.04	0.07
NO ₃ ⁻	1.28	1.45	0.91	4.01	0.47	0.85	14.6	0.35
NH ₄ ⁺	1.11	2.03	0.11	0.33	0.9	20.6	5.46	0.10
OC	45.7	25.1	0	0.54	72.4	9.69	53.8	35.5
EC	30.8	37.6	0.44	0.74	3.11	2.44	3.21	6.7
V	0.13	2.49	0	0	0.09	0	0.06	7.1
Pb	0.55	2.08	0	0	0.04	0	0	13.9
Ni	0	3.42	0	0	0	0	0	0
Na	0	0	38.1	3.93	0	2.09	6.89	0
Cl	0	0	51.9	1.87	0	0	0.4	0
Mn	1.74	0.31	0.14	1.45	0	1.15	1.28	0
Al	1.38	0	0.07	15.8	3.21	0	0	0
Ca	2.67	0	3.73	20.3	0	4.65	5.1	0
Mg	2.09	0.08	3.46	18.4	1.28	0	1.07	0
K	0	4.65	0.07	8.61	2.57	3.46	4.92	12.5
Fe	6.57	0.44	0	18.8	0	1.59	0.45	8.4
Cu	0.88	0	1.02	0	0	0.77	0	17.5

Table 5. Contributions of each source identified with PMF in each category of sampling sites

µg m ⁻³		Traffic	Oil Combustion	Sea Salt	Crustal Material	Secondary Organic	Secondary Sulfate	Secondary Nitrate	Industrial
BE-02	PM ₁₀	4.4 (8.7)	3.8 (7.5)	5.22 (10.3)	10.45 (20.6)	11.81 (23.3)	7.5 (14.8)	5.2 (10.2)	2.4 (4.7)
	PM _{2.5}	2.7 (7.8)	4.1 (11.8)	1.94 (5.6)	3.4 (9.8)	9.27 (26.7)	5.67 (16.4)	4.09 (11.8)	3.5 (10.1)
HE-01	PM ₁₀	10.23 (19.5)		6.45 (12.3)	12.87 (24.6)	8.34 (15.9)	8.1 (15.5)	6.42 (12.2)	
	PM _{2.5}	5.12 (15.6)		2.11 (6.4)	4.54 (13.8)	9.17 (27.9)	6.65 (20.2)	5.32 (16.2)	
SJ-03	PM ₁₀	8.28 (22.7)		4.79 (13.2)	7.63 (21.0)	7.21 (19.8)	4.63 (12.7)	3.87 (10.6)	
	PM _{2.5}	4.04 (18.4)		1.7 (7.7)	2.92 (13.3)	5.83 (26.5)	4.29 (19.5)	3.23 (14.7)	
MO-01	PM ₁₀	7.11 (30.1)		3.42 (14.5)	6.71 (28.4)	0	3.85 (16.3)	2.54 (10.7)	
	PM _{2.5}	4.73 (28.9)		1.85 (11.3)	3.55 (21.7)	0	3.92 (23.9)	2.33 (14.2)	

The third source was characterized with large amounts of Cl^- , Na and Mg, signature of fresh sea salt. These three species, in the four sampling sites, accounted for (51.9–55.3)%, (34.5–38.1)% and 2.9–3.5% of the total mass of this aerosol source, respectively, which is in close agreement with their corresponding percentage composition in seawater. The contribution of this source decreases in average from 10.3% in dry season to 6.1% in rainy season at all the sampling sites, due to wind speed reduction of the Alisios air mass coming from the Caribbean Sea.

The fourth source has large contributions from Al, Ca, Fe and Mg, suggesting crustal or dust aerosols. This is most likely related to exposed soil, unpaved roads and construction activities, as well as other crustal materials. The airborne soil factor accounted for 20.6% and 9.8% of the total PM_{10} and $\text{PM}_{2.5}$ mass concentration in BE-02. Higher contributions were found in the residential site with 28.4% and 21.7% for PM_{10} and $\text{PM}_{2.5}$. Similar to the sea salt, the crustal material contribution showed an average reduction of 46% in rainy season for all the sampling sites.

The fifth source profile was related with secondary organic aerosols and includes OC and sulfate. The OC presented in the source profile, apart from the gas-to-particle conversion of organic gases with relatively low vapor pressure and the chemical processes in cloud and fog droplets provided an alternate explanation that once the secondary inorganic aerosol is formed, the acidic surface could catalyze heterogeneous reactions of organic carbonyl species, leading to potentially multifold increases in secondary organic aerosol mass (Jang et al., 2002). This source contributes with 11.8 and $9.3 \mu\text{g m}^{-3}$ for PM_{10} and $\text{PM}_{2.5}$ concentrations. Lower contributions were obtained for commercial sites may be due to a reduction in volatile organic compound emissions in these sites.

The source 6 assigned to secondary sulfate is traced by sulfate (which accounts for about 60% of the $\text{PM}_{2.5}$ mass in the factor profile) and ammonium. OC is also a major contributor (16%) but it has been found also in other factors. This factor showed high correlation with sulfate ($r=0.71$) and moderate correlation with ammonium ($r=0.57$) for $\text{PM}_{2.5}$ samples. Secondary sulfate was the largest contributor to $\text{PM}_{2.5}$ (24–19%), especially for commercial and residential sites. This factor is often considered as a fingerprint being representative of secondary sulfate (Kim et al., 2004).

The source 7 was determined as secondary nitrate, since nearly the 82% of NO_3^- and OC existed in this factor. The calculated contributions of secondary nitrate to $\text{PM}_{2.5}$ at BE-02 in dry and rainy season were 0.85 and $1.47 \mu\text{g m}^{-3}$ respectively. This temporal behavior can be attributed to the higher stability of ammonium nitrate in warm seasons (Mariani and De Mello, 2007). The observed ratio of $\text{NO}_3^-/\text{NH}_4^+$ for source profile in BE-02 (4.1) is higher than the stoichiometric ratio of $\text{NO}_3^-/\text{NH}_4^+$ for NH_4NO_3 (3.44). This result can be explained through the formation of NaNO_3 and $\text{Ca}(\text{NO}_3)_2$, especially in dry season. Secondary nitrate accounted for 10–12% and 12–16% of total mass in PM_{10} and $\text{PM}_{2.5}$ respectively.

The last source has significant values for Cu, K, Pb and OC. These elements are often emitted from a variety of combustion processes such as heavy fuels. In addition, the presence of K in this mode shows that wood/biomass burning (Cabada et al., 2002) also contributed to this mode. This source contributes with 4.7 and $10.1 \mu\text{g m}^{-3}$ of PM_{10} and $\text{PM}_{2.5}$ mass concentration at industrial site BE-02.

4. Conclusions

The mean annual PM_{10} and $\text{PM}_{2.5}$ concentrations in commercial and industrial sites were higher than Air Quality Standards established by Costa Rican and USA regulations. Results

of PM speciation obtained at the metropolitan area of Costa Rica show that the PM_{10} fraction mainly consists of carbon particles (32.7–59.4%), mineral dust (23.5–35.6%), sea spray (5–8%), and secondary inorganic aerosols (mostly Na, Ca, K, Mg sulfate and nitrate, 20–25%). The $\text{PM}_{2.5}$ fraction mainly comprises OM+EC (44.5–69.9%) with an important fraction of secondary inorganic aerosols (mostly ammonium nitrate and sulfate, 31%) and very minor proportions of mineral dust and sea spray.

Average $\text{PM}_{2.5}$ and PM_{10} OC and EC concentrations during the rainy season were around 1.3–2.4 times higher than dry season. This can be explained by a reduction in the pollution dispersion in the Metropolitan area of Costa Rica during the rainy season. The annual average concentrations of estimated SOC in the Metropolitan Area of Costa Rica contribute with 48% and 56% of the OC in PM_{10} and $\text{PM}_{2.5}$ respectively. There is an overall trend towards lower SOC levels but with a higher percentage of SOC in the TOC at each site during the dry season.

In the same way, crustal matter and sea salt concentrations presented their highest values in dry season due to the influence of Alisios winds that favoring the movement of air masses from Caribbean Sea.

PMF model identified the principal sources of PM_{10} and $\text{PM}_{2.5}$ in each site. Residential site showed a higher traffic and crustal contribution than the industrial site. The PM mass concentrations in BE-02 site are influenced by two additional sources: oil combustion and industrial activities.

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Supporting Material Available

The Supporting Material contains results of SRM 8785 reference material analysis for organic carbon and elemental carbon percentages (Table S1a), Mean OC, EC and TC concentrations obtained at the MACR (Table S1b), Source contribution in each sampling site for $\text{PM}_{2.5}$ samples according to PMF analysis results (Figure S1). This information is available free of charge via the Internet at <http://www.atmospolres.com>.

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