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Temporal and spatial variations in organic and elemental carbon concentrations in $PM_{10}/PM_{2.5}$ in the metropolitan area of Costa Rica, Central America

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ABSTRACT

$PM_{2.5}$ and PM_{10} samples were collected at 4 and 14 sampling sites, respectively, located in the Metropolitan area of Costa Rica (MACR), during 2010–2011. These sites were representative of commercial, industrial and residential zones of this region. Concentrations of elemental carbon (EC) and organic carbon (OC) were analyzed using the IMPROVE thermal–optical reflectance (TOR) method. OC and EC concentrations were higher in commercial and industrial sites and showed clear seasonal variations with higher concentrations observed in the rainy season (May–November) than in the dry season (December–April), due to wind patterns in the study area. Total carbonaceous aerosol accounted for 35% of PM_{10} and 56% of $PM_{2.5}$ mass. Good correlation between OC and EC in PM_{10} (R=0.89–0.75) and $PM_{2.5}$ (R=0.79–0.64) indicated that they had common dominant sources of combustion such as industrial activities and traffic emissions. The annual average concentrations of estimated SOC (Secondary Organic Carbon) in the MACR PM_{10} samples showed values between 0.65–8.49 $\mu g/m^3$, accounting for 48% and 56% of the OC in PM_{10} and $PM_{2.5}$ respectively. Positive Matrix Factorization (PMF) identified five principal sources for OC and EC in particles: gasoline vehicles, diesel vehicles, on road traffic, wood smoke and industrial combustion. The contribution of each of the source varied between the PM_{10} and $PM_{2.5}$ size fractions.

Keywords: *Organic carbon, elemental carbon, aerosol particles, Costa Rica, source apportionment*

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1. Introduction

Atmospheric aerosol is a complex mixture of multicomponent particles that are directly emitted from sources (natural or anthropogenic) and material formed by vapor nucleation/condensation mechanisms, containing elemental and organic carbon, ammonium, nitrates, sulfates, mineral dust, trace elements and water. The study of particle concentrations, sizes and chemical composition at the receptors is essential to elucidate the sources of the aerosols and the processes associated with their formation (Wang et al., 2003; Cheng et al., 2005; Yin and Harrison, 2008; Putaud et al., 2010).

Carbonaceous aerosol constitutes a significant fraction of fine particles, and it could account for up to 40% of $PM_{2.5}$ mass in the urban atmosphere (Seinfeld and Pandis, 1998). Carbonaceous species are usually classified into elemental carbon (EC) and organic carbon (OC). EC is essentially a primary pollutant, emitted directly during the incomplete combustion of carbon–containing fuels. Moreover, the surface of EC particles contains numerous adsorption sites that are capable of enhancing catalytic processes. As the result of its catalytic properties, EC may intervene in some important chemical reactions involving atmospheric sulfur dioxide (SO_2), nitrogen oxides (NO_x), ozone (O_3) and other gaseous compounds (Ho et al., 2002).

OC can be directly emitted from sources (primary OC), or produced from atmospheric reactions, involving gaseous organic precursors (secondary OC). Sources of primary organic carbon are the incomplete combustion of organic materials and the degradation of carbon containing products such as vehicle tires and of vegetation. SOC is formed through the condensation or sorption of organic gases onto particles. Sources of organic gases may be from the combustion of organic material, the evaporation of fuels, or the natural emissions of volatile organic compounds from vegetation. The re–suspension of road dust due to traffic movement may result in increased concentrations of both primary and SOC particulate matter (Jones and Harrison, 2005).

Increasing concerns have been given to carbonaceous aerosol due to its complex impacts on human health (Nel, 2005) and the environment (Ramanathan et al., 2001). EC has a strong absorbtivity of solar radiation and is considered to be the most important particulate component of global warming, whereas OC is mainly a scattering medium and exerts a negative climate forcing influence (Houghton et al., 2001). OC represents a mixture of hundreds of organic compounds, some of which are mutagenic and/or carcinogenic, such as polycyclic aromatic hydrocarbons (PAHs) and polychlorinated dibenzo–p–dioxins and dibenzofurans (PCDD/Fs) (Feng et al., 2006; Li et al., 2008).

MACR contains 75% of the country's vehicle fleet (approximately 734 200 units), 65% of the domestic industry and 60% of the population (2 580 520), according to data from the most recent census (INEC, 2011). The lack of urban planning and population growth in this region of the country during the last 20 years has seriously affected air quality (Herrera and Rodriguez, 2007). The purpose of this paper is to present updated information on the abundance and seasonal characteristics of $PM_{10}/PM_{2.5}$ associated EC and OC in this urban center, such an assessment is needed in investigating the sources and PM control strategies.

2. Experimental

2.1. Sampling

For the PM_{10} and $PM_{2.5}$ sampling, fourteen and four monitoring sites were selected respectively (Table 1). They conform most of the National Air Monitoring Network of Costa Rica. The samplers were placed according to the official Costa Rican regulation No. 30221–S that defines the placement criteria for air quality measurements, and also because they meet essential requirements like security, electricity and access. The sites were also representative of commercial, industrial and residential areas, all located in the MACR, mostly at urban scale (Figure 1). The sampling campaign was conducted between June 2010 and May 2011. Simultaneous samples were collected every six days. To collect PM_{10} samples, Thermo Andersen high volume air samplers with MFC (Mass Flow Controller) were used with a flow rate of 1.13±10% m^3/min. Flow calibration of each sampler was performed by 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, Air Metrics low volume air samplers were used with a flow rate of 5 L/min. The separation of the $PM_{2.5}$ fraction was done at the entrance of the sample by an inlet with two inline impactor stages. The first impactor separated the total PM_{10} size fraction and the second provided for the $PM_{2.5}$ cut point.

In both cases, quartz filters (Whatman CAT No. 1851–865 and Pallflex TYPE:Tissuquartz 2500QAT–UP for PM_{10} and $PM_{2.5}$, respectively) were used for sample collection. Quartz filters were pre–baked at 900 °C for at least 5 hours before use, and stored in Millipore Petrislide dishes covered with plastic and aluminum foil. Samples were collected on a daily basis over 24 hours. Before and after collection, the samples were stored in the freezer and kept frozen during transport. All procedures during handling of filters were strictly quality controlled to avoid any possible contamination.

2.2. Chemical analysis

Samples collected on quartz filters for hi–vol samplers were used for gravimetric analysis in order to determine the $PM_{2.5}$ or PM_{10} concentrations, using a Mettler H31AR analytical balance (0.1 mg resolution). The weighing of the low volume sampler filters was performed using a Mettler MT5 semi–micro analytical balance (0.001 mg resolution). Both balances were calibrated annually and during each weighting session they were checked against certified class E1 weights. A mass concentration uncertainty of ±0.86 μg/m^3 for $PM_{2.5}$ and ±1.22 μg/m^3 for PM_{10} was calculated using a type A evaluation according to the method validation.

Quartz filters were analyzed for OC and EC using a DRI Model 2001 Thermal/Optical Carbon Analyzer (Atmoslytic Inc., Calabasas, CA, USA). A 0.68 cm^2 punch from each filter was analyzed for eight carbon fractions following the IMPROVE TOR protocol (Fung et al., 2002). 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) over a filter blank (pre-heated Quartz filter punch). The 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.

Field blanks for each monitoring site (n=32) and laboratory blanks (n=10) were analyzed to examine potential operational contamination of the field samples. Generally, the concentrations of PM_{10}, $PM_{2.5}$, OC, and EC on the field blanks were less than 1% of the sample batches, and were not subtracted from the samples. Differences between 20 analyzed duplicate samples were less than repeatability limit for the analytical method.

Table 1. *Description of sampling sites and sample collectors used in the OC and EC analysis*

Site	Sampling site type	Municipality	Location	Particle size
SJ–01	Commercial	San Jose	Metropolitan Cathedral Church	PM_{10}
SJ–02	Transition between commercial and residential	San Jose	Transportation Secretary Installations	PM_{10}
SJ–03	Industrial	San Jose	National Electrical Company (CNFL) Office	PM_{10}, $PM_{2,5}$
SJ–04	Transition between commercial and industrial	San Jose	National Register Office	PM_{10}
SJ–05	Residential	San Jose	Communal Recycling Center Building	PM_{10}
HE–01	Commercial	Heredia	National University Central Administration Building	PM_{10}, $PM_{2,5}$
BE–01	Transition between commercial and residential	Belen	La Ribera Commercial Center	PM_{10}
BE–02	Industrial	Belen	Intermodal Company Office	PM_{10}, $PM_{2,5}$
SA–01	Commercial	Santa Ana	MATRA Company Building	PM_{10}
AL–01	Transition between commercial and industrial	Alajuela	National Technical University Campus	PM_{10}
SD–01	Commercial	Santo Domingo	Regional Health Secretary Office	PM_{10}
MO–01	Residential	Moravia	EATON Company Office	PM_{10}, $PM_{2,5}$
CA–01	Industrial	Cartago	Industrial Park	PM_{10}
ES–01	Commercial	Escazu	Escazu Municipality Building	PM_{10}

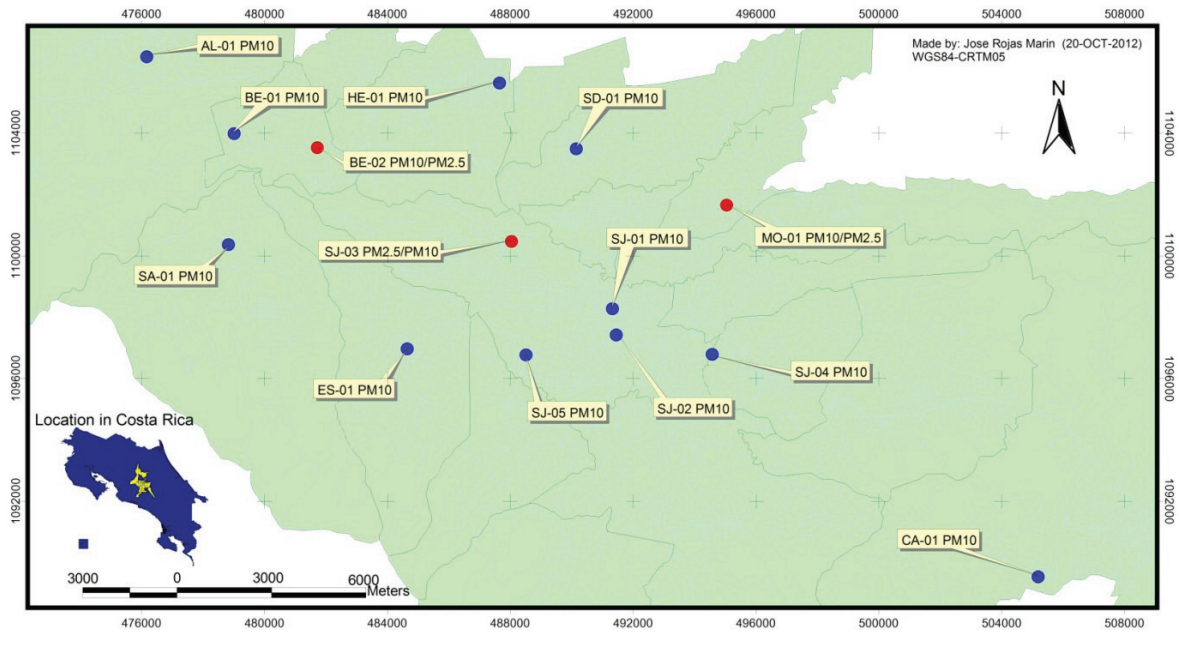

Figure 1. *Sampling sites of PM_{10} and $PM_{2.5}$ concentrations in MACR.*

Table 2. *Results of SRM 8785 reference material analysis for organic carbon and elemental carbon percentages*

	Obtained Values			Reference values SRM 8785		
	% OC	% EC	% TC	% OC	% EC	% TC
N	7	7	7			
Average	0.1085	0.1099	0.2185	0.1120	0.1110	0.2230
Bias	–3.1	–1.0	–2.0			
Standard Deviation	0.0071	0.0248	0.0273	0.0845	0.0335	0.0285

2.3. Quality assurance

NIST 8785 reference material was analyzed in order to evaluate the analytical method accuracy for the determination of organic and elemental carbon in PM_{10}/$PM_{2.5}$. 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 and the results are showed in Table 2. There is not a significant difference between obtained values and reference values, at confidence level of 95%, according to a *t*–test for comparing medians.

2.4. Data analysis

The statistical analysis of the data was performed using a general purpose statistical software package (Minitab®, version 15) running on Windows environment. Multivariate analysis of the data, like Principal Component Analysis (PCA) and Positive Matrix Factorization (PMF), were executed with this software. PCA is a powerful statistical tool that can be used to analyze spatial patterns for several pollutants of interest. Van der Wal and Jansen (2000) have previously shown that PCA can be used to distinguish between large–scale and local phenomena in air pollution analysis.

Positive matrix factorization (PMF) is a bilinear statistical factor analysis model developed by Paatero (1997) which doesn't require source profile knowledge unlike traditional chemical mass balance source–receptor models. Source profiles resolved by PMF were observed to have signatures of localized atmospheric mixing and better represent the local sources, while those identified by Chemical Mass Balance (CMB) are more emission based, which may not be true representations of local characteristics (Lee et al., 2008). Overall, PMF has been identified as a robust source–receptor model and has been used in source apportionment studies of air pollutants including $PM_{2.5}$ (Moon et al., 2008; Fabretti et al., 2009; Lestari and Mauliadi, 2009).

The signal–to–noise ratio (S/N) was used to select the species for further analysis. Species with signal–to–noise (S/N) ratio below 0.2 were classified as bad values according to Paatero (1997) 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 (Paatero, 2000). Missing values were replaced by the geometric mean of the measured values and their accompanying uncertainties were set at four times 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).

2.5. OC and EC emissions inventory development

Estimates of emissions of primary OC and EC in the MACR for 2010 were done in this study. Sources have been classified as

mobile and non–mobile according to the characteristics of their activities.

Mobile sources. ***On–road vehicles***. Emissions from on–road vehicles were determined by multiplying the vehicle kilometers traveled (*VKT*) for each type of vehicle by the corresponding emissions factors. The activity data of the vehicle fleet was taken from a study reported by the Environmental Secretary of Costa Rica (DSE, 2009). Considering the data from the daily trajectory kilometers, the days in use, and the number of vehicles according to the year model distribution; it was possible to calculate the *VKT* for each vehicle type and year model, by the following equation:

$$VKT_{ij} = \left(KT_j\right)\left(NV_{ij}\right)\left(DA_i\right) \quad (1)$$

where VKT_{ij} is the traveled kilometers per vehicle type *i* from model year *j* (km/year), KT_j is the traveled kilometers per day from each vehicle type *i* (km/day), NV_{ij} is the number of vehicles of type *i* from model year *j*, DA_i is the traveled days per year, from vehicles of type *i* (day/year).

The emission factors from organic and elemental carbon were obtained from the software Mobile 6 (USEPA, 2012), which was developed by the USEPA (US Environmental Protection Agency). This software was adapted to specific conditions of Costa Rica, like registration (age) distribution by vehicle class, fuel characteristics, altitude, temperature, roadway type, inspection and maintenance programs, driving cycles and humidity, among others.

Paved Road: Emissions caused by re–suspension of particulate matter from paved roads were calculated based on the following empirical formula (USEPA, 1997):

$$PM_{2.5} = VKT\ k\left(\frac{W}{3}\right)^{1.5}\left(\frac{sL}{2}\right)^{0.65} \quad (2)$$

where *k* is the $PM_{2.5}$ particle size multiplier (g/VMT), *sL* is the road surface silt loading (g/m^2), and *W* is the mean vehicle weight (Mg). The data for *k*, *sL* and *W* were chosen considering the Costa Rica road characteristics. The calculated particle emissions from paved roads were multiplied by the fraction of EC (0.011) and OC (0.14) to obtain the final emission (USEPA, 2002).

Railroad: Railroad emissions in the MACR were calculated by multiplying the amount of diesel sold for railroad operations times the fuel–based emission factor for EC and OC. The emissions for MACR were estimated using the ratio of railway kilometers inside MACR to the total railway miles in Costa Rica. This was the best approach because of the lack of a well established description of the railroad topography as well of emission factors for train engines in Costa Rica, future recalculations can be made when the data become available.

Airplanes: Emissions of EC and OC from airplanes were estimated by multiplying the number of landing and takeoff (LTO) operations by the appropriate emission factor (Turbojet 4 engines EC=1.8 kg C/LTO OC=0.6 kg C/LTO, Turbojet 3 engines EC=0.4 kg C/LTO OC=0.1 kg C/LTO, Turbojet 2 engines EC=0.3 kg C/LTO OC=0.1 kg C/LTO, Turbo prop EC=0.2 kg C/LTO OC=0.1 kg C/LTO) (USEPA, 1997). Data for the total LTO operations and the types of planes at two international airports were obtained from the National Civil Aviation Administration (NCAA, 2010).

Non–mobile sources. ***Combustion sources***. Combustion source emissions of EC and OC were calculated based on fuel consumption reported by Molina (2010) (coal, distillated fuel, residual fuel, natural gas and gasoline) for residential, commercial, industrial and public sectors. Emissions were estimated by the corresponding percentage of EC and OC in the particulate phase by fuel type.

Structural fires: Emissions of OC and EC from structural fires were calculated based on the occurrences of structural fires in the MACR by multiplying the mass of material burned by the carbon emitted per mass of material burned (EC=0.5 Kg C/Ton burned, OC=1.0 kg C/Ton burned) (Turpin and Huntzicker, 1995). Material burned in structural fires and the structural sizes were reported by the National Fire System (NFS, 2012).

Cigarettes: The active population of smokers in the MACR was estimated from data provided by the Ministry of Health. In this region, 18% of the population is active smokers (Health Ministry, 2009). The average smoker in Costa Rica consumes 19 cigarettes a day. Emissions from smoking practices were calculated by multiplying the number of cigarettes consumed times the carbon emission factor (EC=0.01 mg C/cigarette and OC=12 mg C/cigarette) (Hildemann et al., 1991).

3. Results and Discussion

3.1. PM_{10}, $PM_{2.5}$ and OC/EC concentrations

The mean concentrations of the carbon fractions analyzed for each sampling site are given in Table 3, together with the mean PM_{10} and $PM_{2.5}$ mass concentration values obtained at the same time period by the National Air Quality Monitoring Network. The OC/EC and EC/TC ratios were calculated on a sample–by–sample basis and subsequently averaged over all samples of the campaign.

Annual average PM_{10} levels at the different sampling sites ranged from 22 to 56 μg/m^3. PM_{10} annual mass concentrations obtained at high traffic flow commercial zones (HE–01: 56 μg/m^3, SJ–03: 37 μg/m^3 and SJ–05: 35 μg/m^3) and industrial zones (BE–02: 52 μg/m^3) were higher than residential sampling sites. Two sites HE–01 and BE–02 showed values exceeding the Costa Rican Air Quality Annual Standard of 50 μg/m^3 for PM_{10}. From Table 3, it is seen that the mass of $PM_{2.5}$ in all the sampling sites were higher than the USA annualized National Ambient Air Quality Standard (15 μg/m^3). As with PM_{10}, the annual averaged concentrations of $PM_{2.5}$ in high transit commercial and industrial zones were higher (BE–02: 39 μg/m^3) and significantly different at 5% than ones in residential zones (MO–01: 15 μg/m^3). The concentrations of OC and EC, showed similar trend to PM_{10} mass.

Different paired sites (SJ03 vs. BE–02, SJ04 vs. SJ05, SD01 vs. HE–01, HE01 vs. BE–02) showed highly significant Pearson correlation coefficients (p<0.05) that ranged between 0.84 and 0.87 for $PM_{10,}$ and between 0.78 and 0.85 for $PM_{2.5}$ indicating similar temporal associations.

For four sampling sites (HE–01, BE–02, SJ–03 and MO–01), the $PM_{2.5}/PM_{10}$ ratios were calculated on the basis of the data for the $PM_{2.5}$ and PM_{10} samples taken in parallel and then averaged over all samples from the campaign. $PM_{2.5}/PM_{10}$ values were 0.55, 0.58, 0.68 and 0.77 for HE–01, BE–02, SJ–03 and MO–01, respectively. The lower ratios seen in HE–01 and BE–02 reflect high levels of coarse particles due to local industrial activities.

The amount of organic matter in the particles was estimated by multiplying the amount of organic carbon by 1.6 according to Turpin and Lim (2001). Total carbonaceous aerosol (TCA) was calculated by the sum of organic matter and elemental carbon. On average (Table 4), TCA accounted for 35±7% of the PM_{10} with a range of 28–45%. TCA are mainly in the fine fraction and represented on average 56% of the sampled $PM_{2.5}$ mass. EC is mainly emitted by combustion processes and contributes to 29% of the TC in fine and coarse fraction for the sampling sites located in the MACR, whereas OC consists of primary and secondary species from anthropogenic and biogenic origin. EC in the coarse fraction might also come from tire debris or soot deposited on re–suspended dust (Putaud et al., 2004). Whereas, coarse OC may also include biolo-

gical debris (Putaud et al., 2004) in addition to construction, agriculture and natural soil (Chow et al., 1995).

As mentioned in Section 2, eight different temperature resolved fractions can be obtained using the IMPROVE protocol (Chow et al., 1993). The contents of the eight fractions have also been utilized in the source profile study to differentiate gasoline vehicles from diesel vehicles (Watson et al., 1994; Chow et al., 2003) and to differentiate different geological dust (Chow et al., 2004).

The average percentages of carbon fractions for PM_{10} and $PM_{2.5}$ samples collected in the MACR are shown in Figure 2. The average abundances of OC1, OC2, OC3, OC4, EC1–OP, EC2, EC3 and OP in TC were 0.9%, 16.0%, 19.8%, 9.1%, 17.6%, 9.7%, 0.4%, and 26.2% for PM_{10} and 1.5%, 16.0%, 16.6%, 7.1%, 11.1%, 23,4%, 1.06%, 23.2% for $PM_{2.5}$ respectively. Although there were some site–to–site variabilities, OC2, OC3, EC1–OP, and EC2 were generally the most abundant species in PM_{10} and $PM_{2.5}$. There was very little high–temperature (800 °C) EC3 in any of these samples. EC1 accounted for 17.6% of TC in PM_{10} samples, which is higher than that in $PM_{2.5}$ samples (11.1%). EC2 contributed 9.7% for TC in PM_{10} samples, while a much higher contribution (23.4%) of this fraction was found in $PM_{2.5}$. The variation of contributions for EC1 and EC2 in PM_{10} and $PM_{2.5}$ was distinct, which was believed to be due to the catalytic activity of some metals. The metal concentrations in both size fractions can be different. The abundance of metals in samples can lower the soot oxidation temperature and lead to high–temperature soot being measured as low temperature soot in the carbon fraction determination. Therefore, it was reasonable that part of the EC2 from $PM_{2.5}$ was converted to EC1 in PM_{10} when the catalytic activity was promoted by metals (Sternbeck et al., 2002).

3.2. Relation between OC and EC

Since carbonaceous aerosol represents a mixture of various emission sources (EC and primary OC) and secondary OC formed by atmospheric reaction processes, the ratio of OC to EC concentrations (OC/EC) can be used to study the emission and transformation aging characteristics.

As shown in Figure 3, the OC and EC in PM_{10} show a lower concentrations in the dry season (December–April) and higher values in the rainy season (May–November). Comparing the dry season results with those obtained at the same sampling sites during the raining season are lower than those from the dry season shows that the average $PM_{2.5}$ and PM_{10} OC and EC concentrations during the rainy season were around 1.3–2.4 times higher than the dry season. During the dry season, the MACR is affected by winds with speeds close to 30 km/h while in the rainy season, the trade winds decrease their intensity, bringing air from the Pacific, a "front breeze" and causing a reduction in the pollution removal capacity of the MACR. In the same way, temperatures during the rainy season are lower than those from the dry season helping the condensation process that produces secondary organic aerosols.

Strong correlations (*r*) of 0.89–0.75 and 0.79–0.64 were observed for PM_{10} and $PM_{2.5}$ respectively, in all the sampling sites. This indicates that carbonaceous particles in the MACR derived from common emission sources such as vehicular exhaust and/or heavy fuel combustion underwent a similar atmospheric dispersion process.

Even so, the OC/EC ratios displayed some spatial differences as a result of the influence of distinct local emissions. For example, the higher OC/EC ratio values in PM_{10} were found in the sampling sites located in the northwest –southwest region of the MACR (SA–01, AL–01, ES–01, BE–01, BE–02). This zone is located in the region where air normally flows out of the MACR.

Many studies have related the OC/EC ratio to secondary organic particle formation. A primary OC/EC ratio of 2.2 or 2.0 has been usually regarded as an indication of the presence of SOC (Putaud et al., 2004). In other words, the additional OC that causes the OC/EC ratio to exceed 2.2 or 2.0 can be considered to be secondary in origin. According to this hypothesis, SOC might play an important role in carbonaceous pollution in the MACR. Table 2 shows that average OC/EC ratios at the sampling sites ranged from 1.16 to 3.71, for PM_{10} and 1.40–3.96 for $PM_{2.5}$. These values tend to be higher in the rainy season as compared to the dry season.

Table 3. *Mean PM_{10} mass, $PM_{2.5}$ mass, OC, EC and TC concentrations (and associated standard deviations in parentheses) obtained at the MACR*

	SJ–01	SJ–02	SJ–03	SJ–04	SJ–05	HE–01	BE–01	BE–02	SA–01	AL–01	SD–01	MO–01	CA–01	ES–01
							PM_{10}							
N	30	32	36	38	31	37	41	43	35	34	32	33	32	31
Mass Concentration ($\mu g/m^3$)	28 (8)	26 (9)	37 (11)	29 (9)	35 (15)	56 (23)	34 (16)	52 (19)	26 (9)	25 (12)	22 (8)	22 (7)	28 (13)	22 (11)
OC ($\mu g/m^3$)	3.09 (1.63)	4.09 (1.54)	4.69 (2.85)	5.09 (1.88)	5.87 (3.40)	13.45 (9.44)	6.34 (2.63)	7.51 (2.92)	4.92 (2.31)	5.23 (2.17)	4.69 (2.41)	4.27 (2.56)	4.52 (1.92)	4.53 (1.19)
EC ($\mu g/m^3$)	2.98 (2.08)	1.35 (0.51)	3.97 (2.38)	2.11 (0.69)	2.00 (0.64)	3.54 (1.42)	2.42 (0.63)	2.61 (0.69)	1.50 (0.47)	1.68 (0.64)	1.61 (0.60)	1.36 (0.70)	1.22 (0.32)	1.50 (0.32)
TC ($\mu g/m^3$)	6.07 (3.60)	5.44 (1.92)	8.66 (4.00)	7.19 (2.03)	7.88 (3.80)	16.99 (10.56)	8.75 (3.13)	10.12 (3.40)	6.42 (2.72)	6.91 (2.72)	6.29 (2.60)	5.63 (3.10)	5.73 (2.17)	6.03 (1.48)
OC/EC	1.16	3.13	1.18	2.27	2.91	3.45	2.60	2.89	3.20	3.18	2.73	3.41	3.71	3.01
EC/TC	0.48	0.25	0.46	0.30	0.27	0.27	0.29	0.27	0.24	0.24	0.30	0.24	0.22	0.25
							$PM_{2.5}$							
N			34			38		35				34		
Mass Concentration ($\mu g/m^3$)			25 (16)			31 (23)		30 (17)				17 (9)		
OC ($\mu g/m^3$)			5.73 (1.88)			10.09 (4.67)		9.12 (2.90)				4.45 (2.08)		
EC ($\mu g/m^3$)			4.50 (1.68)			4.11 (2.27)		2.30 (0.51)				1.37 (1.10)		
TC ($\mu g/m^3$)			9.27 (2.50)			14.20 (6.77)		11.42 (3.32)				5.82 (2.81)		
OC/EC			1.38			2.51		3.96				3.25		
EC/TC			0.48			0.29		0.21				0.2		

Table 4. *Levels of SOC and POC obtained for PM_{10} and $PM_{2.5}$ samples in the MACR*

Sampling Site	TCA (µg/m^3)	TCA/PM	SOC (µg/m^3)	POC (µg/m^3)
		PM_{10}		
SJ–01	7.92	0.28	0.65	2.44
SJ–02	7.89	0.30	1.47	2.61
SJ–03	11.47	0.31	2.18	2.50
SJ–04	10.25	0.35	2.40	2.69
SJ–05	11.39	0.32	4.60	1.27
HE–01	25.06	0.45	8.49	4.96
BE–01	12.56	0.37	2.93	3.40
BE–02	14.63	0.28	3.17	4.34
SA–01	9.37	0.36	1.79	3.14
AL–01	10.05	0.40	1.68	3.55
SD–01	9.11	0.41	2.54	2.15
MO–01	8.19	0.37	1.76	2.60
CA–01	8.45	0.30	1.87	2.64
ES–01	8.75	0.40	1.02	3.52
		$PM_{2.5}$		
SJ–03	13.67	0.55	2.31	3.42
HE–01	20.25	0.65	7.01	3.38
BE–02	16.89	0.56	3.78	5.34
MO–01	8.49	0.50	2.67	1.78

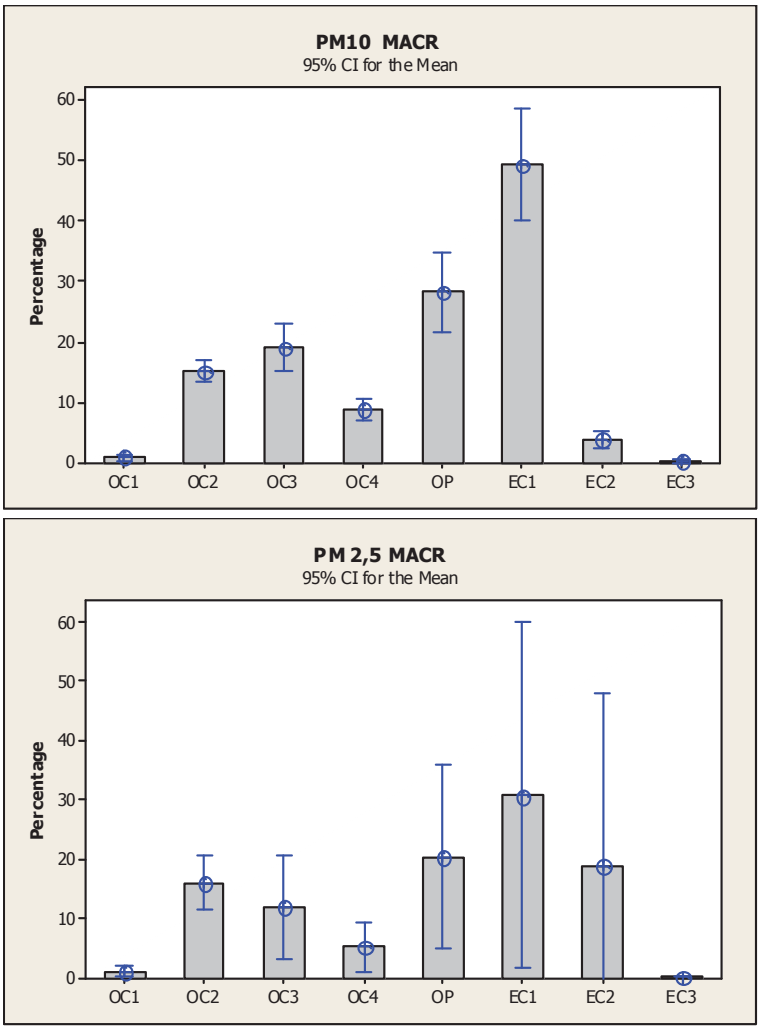

Figure 2. *Average percentages of the eight carbon fractions that contribute to total carbon in PM_{10} and $PM_{2.5}$ samples in the MACR.*

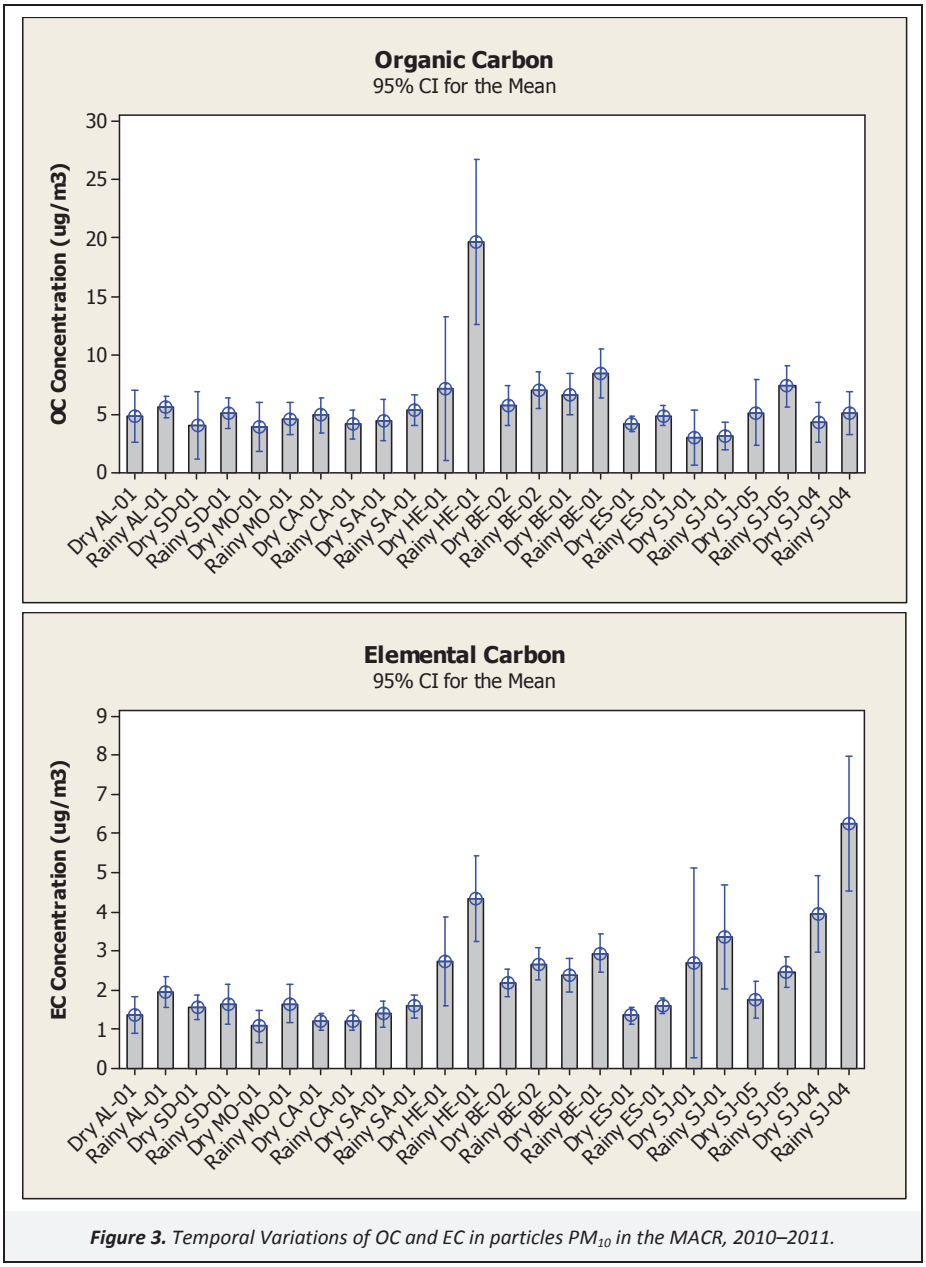

Figure 3. *Temporal Variations of OC and EC in particles PM_{10} in the MACR, 2010–2011.*

3.3. Abundances of SOC and POC

OC consists of a complicated mixture of species from both primary and secondary sources. The separation and quantification of primary and secondary OC is of great importance in under–standing secondary aerosol formation as well as in controlling particulate carbon pollution. The separation and quantification of primary and secondary OC have been difficult to achieve. Because no simple, direct analytical technique is available, an indirect method was used. Since EC is predominantly emitted from primary combustion sources, it has often been used as a tracer of primary OC in evaluation of the SOC concentrations. The ratio of OC/EC in source emissions when compared to the same ratio in atmospheric samples is believed to be indicative of the presence of secondary organic aerosol (SOA) formation. In the EC tracer method (Turpin and Huntzicker, 1995; Yu et al., 2004; Yu et al., 2007), SOC is esti-mated by means of the following equation:

$$SOC = OC_{tot} - EC\left(\frac{OC}{EC}\right)prim \quad (3)$$

where *SOC* is the secondary OC, and OC_{tot} 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) primary has been represented by the observed minimum ratio [(OC/EC)min], and assumptions regarding the use of this procedure as were discussed in detail by Castro et al. (1999).

The annual average concentrations of estimated PM_{10} SOC in the MACR (Table 4) ranged between 0.65 to 8.49 μg/m^3, accounting for 48% and 56% of the OC in PM_{10} and $PM_{2.5}$ respectively.

Compared with rainy season results, there is an overall trend toward lower SOC levels but with a higher percentage of SOC in the TOC at each site during the dry season (Figure 4). Higher tempera-tures and more intense solar radiation during the summer months provide favorable conditions for photochemical activity and SOC production.

3.4. Source identification for OC and EC

Principal Component Analysis (PCA) has been carried out to analyze spatial patterns in the TC PM_{10} concentration over the MACR. Van der Wal and Janssen (2000) have previously shown that PCA can be used to distinguish between large–scale and local phenomena in air pollution analysis. PCA was applied to analyze the concentration patterns of the different types of PM from the different measurement stations. Table 5 summarizes the results for PM_{10} data during the sampling period. The first principal component explains 32.7% of the total variance and includes commercial sites with medium–high traffic (HE–01, SJ–02, SJ–03, SJ–04 and SJ–05). The second component takes into account the industrial, residential and commercial sampling sites (SA–01, ES–01, AL–01, BE–01 and BE–02) located at the northwest in the wind exit zone of the MACR. The third and fourth components, explain 15.8 and 5.6% of the total variance, respectively. Residential and commercial sites with low traffic (SJ–01, MO–01 and SD–01) are integrated in the third component. At the end, CA–01 is the unique sampling site included in the fourth factor.

PMF, described previously in Section 2.4 was applied using the data of the different temperature resolved fractions of organic and elemental carbon concentrations obtained for the samples of $PM_{2.5}$ and PM_{10} particles (at the four groups of sampling sites) collected in the MACR, in order to obtain the fractional carbon profiles for combustion sources. Table 6 shows the PMF results for these groups.

Three different traffic–related combustion factors were identified in this study: gasoline vehicles accounting for 10% of the $PM_{2.5}$ mass concentration, on–road diesel emissions accounting for 16%, and railroad traffic accounting for 4%. They are represented by high carbon fractions whose abundances differ among the sources. As shown in Table 6, gasoline vehicle emissions have high concentrations of OC fractions. The gasoline vehicle source has large amounts of OC3 and OC4. The source identified as on–road diesel emissions contains high concentrations of EC1 and OC2. The ''railroad'' profile source is represented by high EC2 concentration. The other two possible sources that were obtained are wood smoke (containing high concentrations of OC2 and OC3) and industrial combustion (Lowenthal et al., 1994; Watson et al., 2001; Watson and Chow, 2001). These sources contribute 5 and 9% of $PM_{2.5}$ mass concentration, respectively.

Some differences are observed when source contributions are compared for the three categories of PM_{10} sampling sites (Figure 5). For example, for PM_{10} commercial sites, four principal sources were identified by PMF: gasoline vehicles, diesel vehicles, on–road traffic and industrial combustion accounting for 9, 13, 7 and 6% respectively. In the case of PM_{10} residential category, only gasoline vehicles, diesel vehicles and on–road traffic contributes to PM_{10} mass. This means that traffic emissions are predominant in these sampling sites.

3.5 Emissions inventory for OC and EC

Table 7 summarizes the particulate EC and OC primary emissions by source categories for the MACR. The $PM_{2.5}$ inventory for the area includes a contribution of 8 140 tons/year from OC and 2 518 tons/year from EC. On an annual basis, the major sources of primary OC emissions are industrial combustion (92.3%), diesel vehicles (3.51%) and gasoline vehicles (2.65%). On an annual basis, the major EC sources are industrial combustion (74.7%), diesel vehicles (15.7%), residential combustion (5.4%) and gasoline vehicles (1.22%). As can be seen, the sources identified by PMF show a good agreement with the emission inventory.

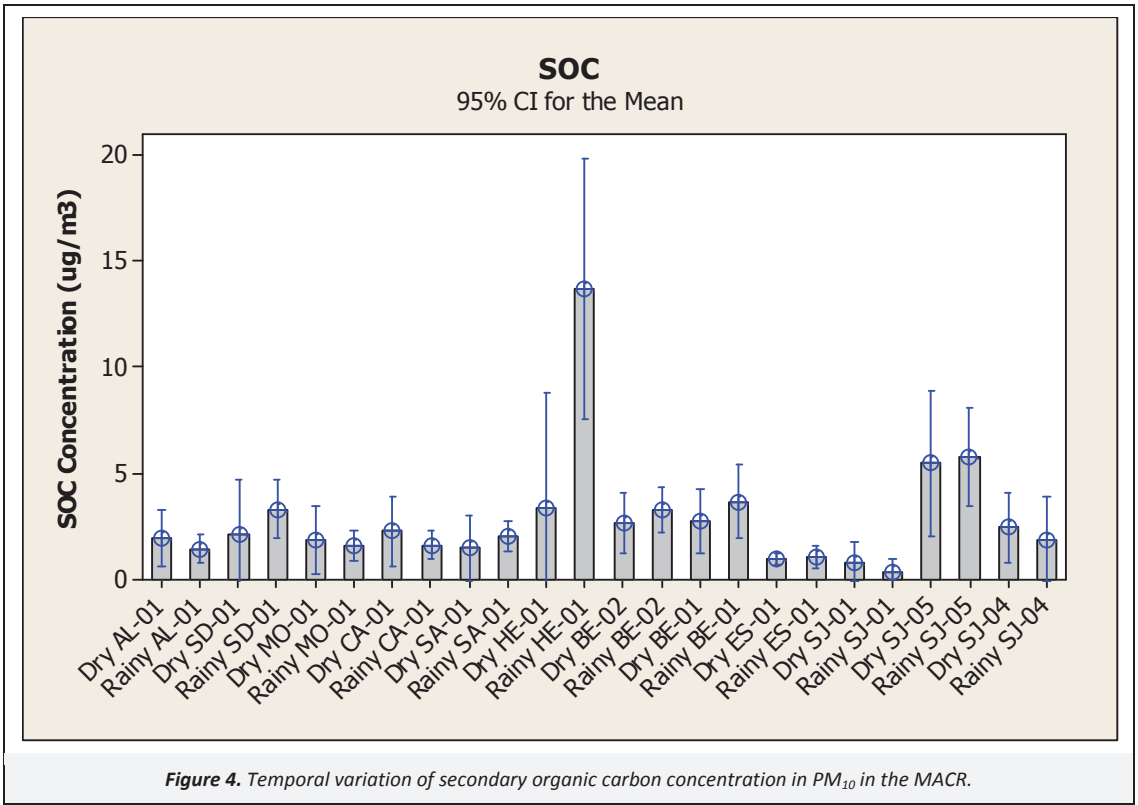

Figure 4. *Temporal variation of secondary organic carbon concentration in PM_{10} in the MACR.*

Table 5. *Results of principal component analysis using TC PM_{10} data in the MACR, 2010–2011*

	PC1	PC2	PC3	PC4
AL–01	0.102	**0.736**	0.091	0.177
SD–01	0.053	0.011	**0.924**	0.244
MO–01	–0.087	0.067	**0.789**	–0.133
CA–01	0.243	0.131	–0.264	**0.673**
SA–01	0.207	**0.558**	–0.105	–0.298
HE–01	**0.718**	0.174	0.212	0.019
BE–01	0.125	**0.652**	0.049	0.128
BE–02	0.096	**0.606**	0.117	0.093
ES–01	0.188	**0.509**	0.139	0.275
SJ–01	0.249	0.227	**0.542**	0.102
SJ–02	**0.498**	–0.134	0.067	0.209
SJ–05	**0,624**	0.085	0.385	0.185
SJ–03	**0.723**	0.229	0.254	0.076
SJ–04	**0.556**	0.133	0.302	0.172
Eigen Value	**3.3545**	**2.5920**	**1.7745**	**1.2942**
Explained Variance (%)	**32.7**	**23.9**	**15.8**	**5.6**

Table 6. *Source profiles (µg/µg) derived by PMF for $PM_{2.5}$ and PM_{10} samples collected in the MACR*

	$PM_{2.5}$					PM_{10} high traffic commercial sites				PM_{10} northwest sampling sites				PM_{10} Residential Sampling sites		
Sources	01	02	03	04	05	02	03	04	05	02	03	04	05	02	03	04
OC1	0.078	0.027	0.049	0.031	0.012	0.003	0.019	0.035	0.003	0.017	0.054	0.043	0.007	0.001	0.017	0.003
OC2	0.127	0.146	0.187	0.096	0.088	0.109	0.173	0.088	0.072	0.125	0.177	0.105	0.084	0.088	0.147	0.051
OC3	0.158	0.295	0.069	0.145	0.119	0.197	0,044	0.114	0.083	0.221	0,052	0.123	0.095	0.145	0,032	0.099
OC4	0.018	0.196	0.094	0.009	0.156	0.165	0.079	0.001	0.092	0.174	0.085	0.004	0.118	0.102	0.064	0.002
OP	0.040	0.032	0.001	0.001	0.017	0.034	0.022	0.008	0.002	0.019	0.016	0.009	0.014	0.013	0.008	0.008
EC1	0.030	0.078	0.087	0.048	0.177	0.061	0.071	0.031	0.146	0.081	0.079	0.037	0.160	0.055	0.086	0.038
EC2	0.009	0.045	0.195	0.323	0,204	0.029	0.141	0.246	0.167	0.036	0.164	0.259	0.173	0.032	0.148	0.134
EC3	0.003	0.019	0.008	0.089	0.064	0.014	0.032	0.101	0.042	0.010	0.025	0.098	0.056	0.010	0.008	0.056

01: Wood smoke, 02: Gasoline vehicle, 03: On road diesel emissions, 04: Rail road traffic, 05: Industrial combustion

Table 7. *Carbon emissions inventory for the MACR in 2010*

Source	Primary OC (ton/year)	(%)	Primary EC (ton/year)	(%)
Mobile Sources				
Gasoline vehicles				
Automobiles	213.4	2.62	29.51	1.17
Taxis	2.58	0.03	1.15	0.05
Diesel vehicles				
Taxi	1.45	0.02	5.07	0.20
Bus	27.91	0.34	35.49	1.41
Heavy Trucks	117.25	1.44	147.76	5.87
Light Trucks	118.69	1.46	148.94	5.91
Light Cars	20.04	0.25	57.74	2.29
Non Mobile Sources				
Airplanes	16.03	0.20	40.33	1.60
Residential Combustion	92.1	1.13	135	5.36
Commercial Combustion	0.82	0.01	0.87	0.03
Industrial Combustion	7 510	92.26	1 880	74.66
Agriculture Combustion	0.96	0.01	1.1	0.04
Structural Fires	1.61	0.02	0.81	0.03
On road vehicles	17.14	0.21	1.35	0.05
Cigarettes	0.026	0.00	32.9	1.31
Total	**8 140**		**2 518**	

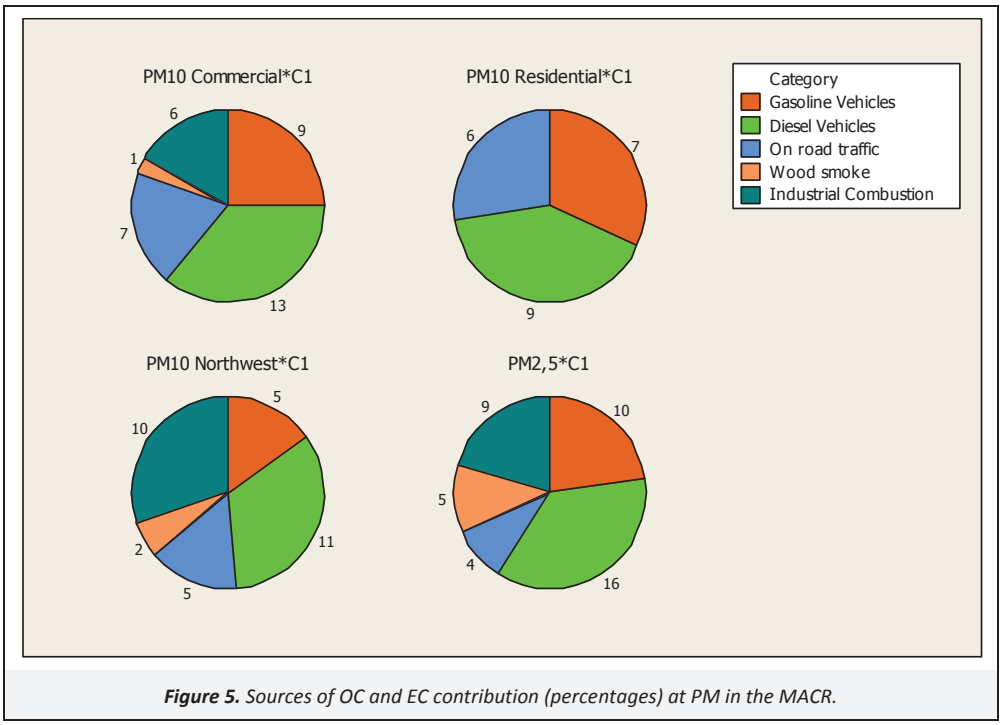

Figure 5. *Sources of OC and EC contribution (percentages) at PM in the MACR.*

4. Conclusions

Annual average PM_{10} and $PM_{2.5}$ and the OC and EC in both fractions, showed higher values in commercial zones with high traffic flow and industrial activity than residential sites. On average, TCA accounted for 35±7% of the PM_{10} and 56% of the sampled $PM_{2.5}$ mass. The majority of ambient PM_{10} OC and EC were observed to be associated with $PM_{2.5}$. The estimated EC contributes 29% of the TC in fine and coarse fraction for the sampling sites.

The OC and EC in PM_{10} and $PM_{2.5}$ show lower concentrations in the dry season (December–April) and higher values in the rainy season (May–November) since during the dry season the MACR is affected by winds with speeds close to 30 km/h while in the rainy season, the trade winds decrease their intensity, causing a reduction in the pollution removal capacity in the MACR. The higher OC/EC ratios in PM_{10} were found in the sampling sites located in the northwest –southwest region of the MACR (SA–01, AL–01, ES–01, BE–01, BE–02). This zone is located in the region of the MACR where air masses normally flow out of the city.

SOC accounted for 48% and 56% of the OC in PM_{10} and $PM_{2.5}$ respectively. Compared with the rainy season results, in the dry season there is an overall trend toward lower SOC levels but with a higher percentage of SOC in the TOC. Higher temperatures and more intense solar radiation during the summer months provide favorable conditions for photochemical activity and SOC production.

Five different sources were identified in this study for OC and EC in $PM_{2.5}$: gasoline vehicles accounting for 10% of the $PM_{2.5}$ mass concentration, on–road diesel emissions accounting for 16%, railroad traffic accounting for 4%, wood smoke (containing high concentrations of OC2 and OC3) and industrial combustion. These sources contribute with 5 and 9% of $PM_{2.5}$ mass concentration. These results are similar to the emission data obtained from the MACR OC and EC Emission Inventory conducted in this study.

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References

Castro, L.M., Pio, C.A., Harrison, R.M., Smith, D.J.T., 1999. Carbonaceous aerosol in urban and rural European atmospheres: estimation of secondary organic carbon concentrations. *Atmospheric Environment* 33, 2771-2781.

Cheng, M.T., Lin, Y.C., Chio, C.P., Wang, C.F., Kuo, C.Y., 2005. Characteristics of aerosols collected in central Taiwan during an Asian dust event in spring 2000. *Chemosphere* 61, 1439-1450.

Chow, J.C., Watson, J.G., Kuhns, H., Etyemezian, V., Lowenthal, D.H., Crow, D., Kohl, S.D., Engelbrecht, J.P., Green, M.C., 2004. Source profiles for industrial, mobile, and area sources in the big bend regional aerosol visibility and observational study. *Chemosphere* 54, 185-208.

Chow, J.C., Watson, J.G., Ashbaugh, L.L., Magliano, K.L., 2003. Similarities and differences in PM_{10} chemical source profiles for geological dust from the San Joaquin Valley, California. *Atmospheric Environment* 37, 1317-1340.

Chow, J.C., Fairley, D., Watson, J.G., Demandel, R., Fujita, E.M., Lowenthal, D.H., Lu, Z.Q., Frazier, C.A., Long, G., Cordova, J., 1995. Source apportionment of wintertime PM_{10} at San-Jose, Calif. *Journal of Environmental Engineering-ASCE* 121, 378-387.

Chow, J.C., Watson, J.G., Pritchett, L.C., Pierson, W.R., Frazier, C.A., Purcell, R.G., 1993. The DRI thermal optical reflectance carbon analysis system - description, evaluation and applications in United-States air-quality studies. *Atmospheric Environment Part A-General Topics* 27, 1185-1201.

DSE, 2009. Annual Average vehicle movement in Costa Rica, Environment and Energy Ministry, Energy Sector Office, 142 pages.

Fabretti, J.F., Sauret, N., Gal, J.F., Maria, P.C., Scharer, U., 2009. Elemental characterization and source identification of $PM_{2.5}$ using positive matrix factorization: the Malraux road tunnel, Nice, France. *Atmospheric Research* 94, 320-329.

Feng, J.L., Chan, C.K., Fang, M., Hu, M., He, L.Y., Tang, X.Y., 2006. Characteristics of organic matter in $PM_{2.5}$ in Shanghai. *Chemosphere* 64, 1393-1400.

Fung, K., Chow, J.C., Watson, J.G., 2002. Evaluation of OC/EC speciation by thermal manganese dioxide oxidation and the improve method.

Journal of the Air and Waste Management Association 52, 1333-1341.

Health Ministry, 2009. Report on Smoking Habits, MS, San José.

Herrera, J., Rodríguez, S., 2007. Fourth San Jose Air Quality Report (2007) Tecnhical Report, pp. 15-16 (in Mexican).

Hildemann, L.M., Markowski G.R., Cass G.R., 1991. Chemical composition of emissions from urban sources of fine organic aerosol. *Environmental Science and Technology* 25, 744-759.

Ho, K.F., Lee, S.C., Yu, J.C., Zou, S.C., Fung, K., 2002. Carbonaceous characteristics of atmospheric particulate matter in Hong Kong. *Science of the Total Environment* 300, 59-67.

Hopke, P.K., Paatero, P., 2002. Discarding or downweighing high-noise variables in factor analytic models. *Annual Conference of the American Association for Aerosol Research*, Charlotte, NC.

Houghton, J. T., Ding, Y., Griggs, D. J., Noguer, M., van der Linden, P. J., Dai, X., 2001. IPCC, 2001: Climate Change 2001: The Scientific Basis. Contribution of Working Group I to the Third Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge, 94 pages.

INEC (Instituto Nacional de Estadística y Censos de Costa Rica), 2011. National Population Census. Preliminar Report, San Jose, 67 pages.

Jones, A.M., Harrison, R.M., 2005. Interpretation of particulate elemental and organic carbon concentrations at rural, urban and kerbside sites. *Atmospheric Environment* 39, 7114-7126.

Lee, S., Liu, W., Wang, Y.H., Russell, A.G., Edgerton, E.S., 2008. Source apportionment of $PM_{2.5}$: comparing PMF and CMB results for four ambient monitoring sites in the Southeastern United States. *Atmospheric Environment* 42, 4126-4137.

Lestari, P., Mauliadi, Y.D., 2009. Source apportionment of particulate matter at urban mixed site in Indonesia using PMF. *Atmospheric Environment* 43, 1760-1770.

Li, H.R., Feng, H.L., Sheng, G.Y., Lu, S.L., Fu, J.M., Peng, P.A., Man, R., 2008. The PCDD/F and PBDD/F pollution in the ambient atmosphere of Shanghai, China. *Chemosphere* 70, 576-583.

Lowenthal, D.H., Zielinska, B., Chow, J.C., Watson, J.G., Gautam, M., Ferguson, D.H., Neuroth, G.R., Stevens, K.D., 1994. Characterization of heavy-duty diesel vehicle emissions. *Atmospheric Environment* 28, 731-743.

Molina, A., 2010. National Energy Balance 2009, Environment and Energy Ministry, San José (in Mexican).

Moon, K.J., Han, J.S., Ghim, Y.S., Kim, Y.J., 2008. Source apportionment of fine carbonaceous particles by positive matrix factorization at Gosan background site in East Asia. *Environment International* 34, 654-664.

NCAA (National Civil Aviation Administration), 2010. Statistical Yearbook 2009. DGAC, San Jose.

NFS (National Fire System), 2012. Personal communication, May 14, 2012.

Nel, A., 2005. Air pollution-related illness: effects of particles (vol 308, pg 804, 2005). *Science* 309, 1326-1326.

Paatero, P., 2000. User's guide for positive matrix factorization programs PMF2 and PMF3, Part 1: tutorial.

Paatero, P., 1997. Least squares formulation of robust non-negative factor analysis. *Chemometrics and Intelligent Laboratory Systems* 37, 23-35.

Polissar, A.V., Hopke, P.K., Poirot, R.L., 2001. Atmospheric aerosol over vermont: chemical composition and sources. *Environmental Science and Technology* 35, 4604–4621.

Putaud, J.P., Van Dingenen, R., Alastuey, A., Bauer, H., Birmili, W., Cyrys, J., Flentje, H., Fuzzi, S., Gehrig, R., Hansson, H.C., Harrison, R.M., Herrmann, H., Hitzenberger, R., Huglin, C., Jones, A.M., Kasper-Giebl, A., Kiss, G., Kousa, A., Kuhlbusch, T.A.J., Loschau, G., Maenhaut, W., Molnar, A., Moreno, T., Pekkanen, J., Perrino, C., Pitz, M., Puxbaum, H., Querol, X., Rodriguez, S., Salma, I., Schwarz, J., Smolik, J., Schneider, J., Spindler, G., ten Brink, H., Tursic, J., Viana, M., Wiedensohler, A., Raes, F., 2010. A European aerosol phenomenology-3: physical and chemical characteristics of particulate matter from 60 rural, urban, and kerbside sites across Europe. *Atmospheric Environment* 44, 1308-1320.

Putaud, J.P., Raes, F., Van Dingenen, R., Bruggemann, E., Facchini, M.C., Decesari, S., Fuzzi, S., Gehrig, R., Huglin, C., Laj, P., Lorbeer, G., Maenhaut, W., Mihalopoulos, N., Mulller, K., Querol, X., Rodriguez, S., Schneider, J., Spindler, G., ten Brink, H., Torseth, K., Wiedensohler, A., 2004. European aerosol phenomenology-2: chemical characteristics of particulate matter at kerbside, urban, rural and background sites in Europe. *Atmospheric Environment* 38, 2579-2595.

Ramanathan, V., Crutzen, P.J., Kiehl, J.T., Rosenfeld, D., 2001. Atmosphere - aerosols, climate, and the hydrological cycle. *Science* 294, 2119-2124.

Seinfeld, J.H., Pandis, S.N., 1998. *Atmospheric Chemistry and Physics: from Air Pollution to Climate Change*, Wiley, New York, 1326 pages.

Sternbeck, J., Sjodin, A., Andreasson, K., 2002. Metal emissions from road traffic and the influence of resuspension - results from two tunnel studies. *Atmospheric Environment* 36, 4735-4744.

Turpin, B.J., Lim, H.J., 2001. Species contributions to $PM_{2.5}$ mass concentrations: revisiting common assumptions for estimating organic mass. *Aerosol Science and Technology* 35, 602-610.

Turpin, B.J., Huntzicker, J.J., 1995. Identification of secondary organic aerosol episodes and quantitation of primary and secondary organic aerosol concentrations during SCAQS. *Atmospheric Environment* 29, 3527-3544.

USEPA (U.S. Environmental Protection Agency), 2012. MOBILE6 vehicle emission modeling software, Washington, DC,

USEPA (U.S. Environmental Protection Agency), 1997. Emission Inventory Improvement Program (EIIP) Technical Report Series, Volumes 1-10, EPA-454/R-97-004a-g, Washington, DC.

Van der Wal, J.T., Janssen, J.M. 2000. Analysis of spatial and temporal variations of PM_{10} concentrations in the Netherlands using Kalman filtering. *Atmospheric Environment* 34, 3675-3687.

Wang, G.H., Wang, H., Yu, Y.J., Gao, S.X., Feng, J.F., Gao, S.T., Wang, L.S., 2003. Chemical characterization of water-soluble components of PM_{10} and $PM_{2.5}$ atmospheric aerosols in five locations of Nanjing, China. *Atmospheric Environment* 37, 2893-2902.

Watson, J.G., Chow, J.C., 2001. Source characterization of major emission sources in the imperial and Mexicali valleys along the US/Mexico border. *Science of the Total Environment* 276, 33-47.

Watson, J.G., Chow, J.C., Houck, J.E., 2001. $PM_{2.5}$ chemical source profiles for vehicle exhaust, vegetative burning, geological material, and coal burning in Northwestern Colorado during 1995. *Chemosphere* 43, 1141-1151.

Watson, J.G., Chow, J.C., Lowenthal, D.H., Pritchett, L.C., Frazier, C.A., Neuroth, G.R., Robbins, R., 1994. Differences in the carbon composition of source profiles for diesel-powered and gasoline-powered vehicles. *Atmospheric Environment* 28, 2493-2505.

Yin, J.X., Harrison, R.M., 2008. Pragmatic mass closure study for $PM_{1.0}$, $PM_{2.5}$ and PM_{10} at roadside, urban background and rural sites. *Atmospheric Environment* 42, 980-988.

Yu, S., Bhave, P.V., Dennis, R.L., Mathur, R., 2007. Seasonal and regional variations of primary and secondary organic aerosols over the continental United States: semi-empirical estimates and model evaluation. *Environmental Science and Technology* 41, 4690-4697.

Yu, S.C., Dennis, R.L., Bhave, P.V., Eder, B.K., 2004. Primary and secondary organic aerosols over the United States: estimates on the basis of observed organic carbon (OC) and elemental carbon (EC), and air quality modeled primary OC/EC ratios. *Atmospheric Environment* 38, 5257-5268.