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## Levels, composition and source apportionment of rural background PM<sub>10</sub> in western Mexico (state of Colima)

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### ABSTRACT

The variability of levels and composition of PM<sub>10</sub> were investigated (October 2006 to May 2007) in a semi-rural classified site located in the central region of the state of Colima (Western Mexico), away from the direct influence of pollution sources. Mean PM<sub>10</sub> levels reached relatively high values (48 µg/m<sup>3</sup>), due mainly to enhanced loads of crustal material (15 µg/m<sup>3</sup>), carbonaceous aerosols (10 µg/m<sup>3</sup>) and sulfate (9 µg/m<sup>3</sup>). Dust resuspension, volcanic, industrial, agricultural, farming, and road traffic emissions, as well as regional pollution were identified as the main drivers of this variability. Furthermore, meteorological factors at local, regional and synoptic scales influenced such PM<sub>10</sub> variability. A differentiation was found between the cold period, with average PM<sub>10</sub> levels reaching 42 µg/m<sup>3</sup>, and the warm period, with 56 µg/m<sup>3</sup>. The first study period was characterized by high levels of SO<sub>4</sub><sup>2-</sup> (19 µg/m<sup>3</sup>) arising from both anthropogenic and volcanic emissions, whereas the second one is characterized by a high contribution from crustal material (22 µg/m<sup>3</sup>) from soil resuspension and volcanic ash. Principal component analysis (PCA) showed that the highest contribution to PM<sub>10</sub> levels arises from the regional pollution (49%), followed by the industrial emissions, fuel oil combustion, road traffic and secondary sulfate (18, 17, 10 and 6%, respectively). This shows a large anthropogenic load in rural background PM pollution, consequently, we propose to build an air quality monitoring network in rural and urban areas of this region.

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### 1. Introduction

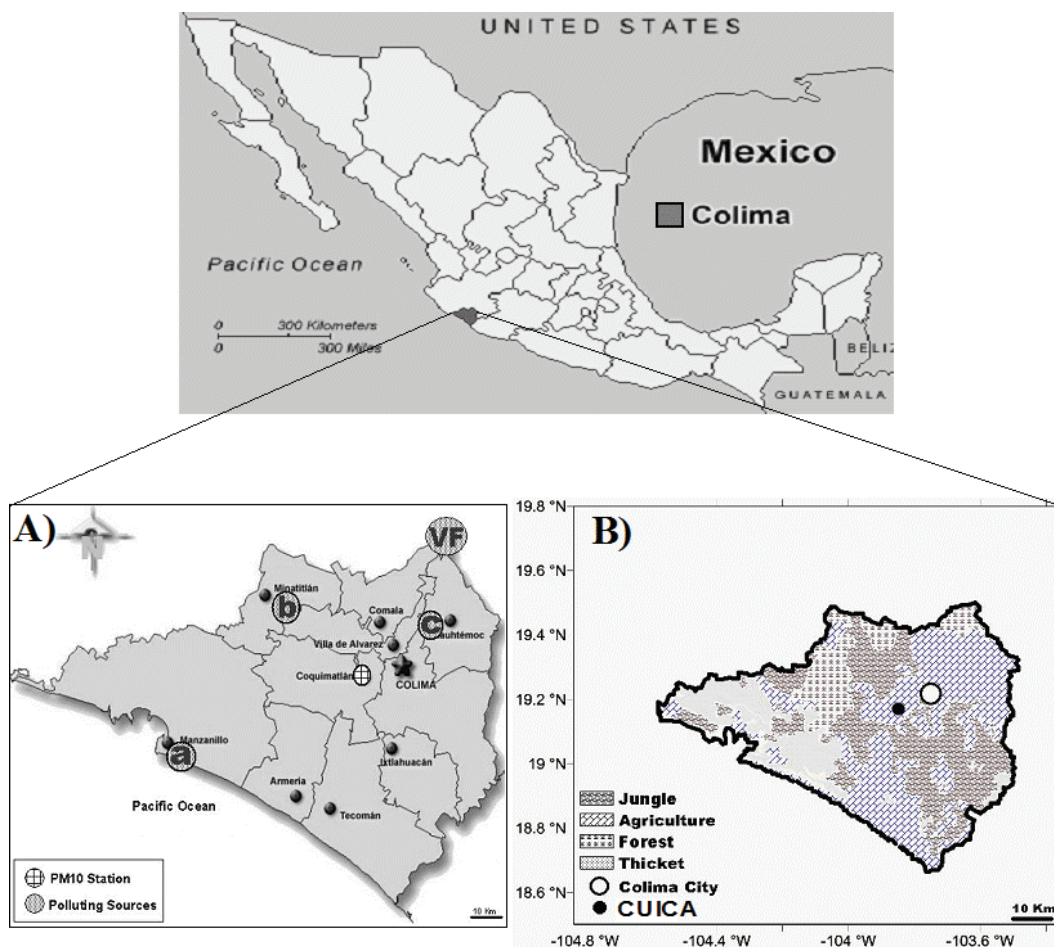
Atmospheric particles having a diameter of less than 10 µm (PM<sub>10</sub>) consist of solid and/or liquid particles that are incorporated into the atmosphere by natural and anthropogenic emission sources. Atmospheric processes and multi-source origin tend to generate a complex mixture of aerosol components of different chemical and physical characteristics.

Primary particles are directly released into the atmosphere. Secondary particles are formed within the atmosphere by gas-to-particle conversion from gaseous precursors such as sulfur dioxide (SO<sub>2</sub>), nitrogen dioxide (NO<sub>2</sub>), ammonia (NH<sub>3</sub>) and volatile organic compounds. Moreover, some studies have shown that suspended air particles are associated with different types of sources, and that their origin (metallurgical, foundry, steel, chemical industry or vehicle emissions) can be traced based on their microscopic morphology and chemical composition (Aragon et al., 2006).

It is widely accepted that high concentrations of ambient air particles cause adverse health effects on humans (Dockery et al., 1996; Donaldson and MacNee, 1998; Donaldson et al., 2000; Pope et al., 2002; WHO, 2005), such as asthma problems in children (Lee et al., 2006). Furthermore, a number of ecological effects (negative and positive) caused by the presence of atmospheric particles have been reported (Grantz et al., 2003).

The state of Colima (Western Mexico, Figure 1), one of the smaller states of the country with only 0.3% of the total area (5 455 km<sup>2</sup>), has shown an important population growth (650 555 inhabitants in 2010) and economic development in last few years mainly related to the expansion of the industrial, agricultural and cattle breeding sectors (INEGI, 2005). As a consequence, Colima's air quality has been progressively influenced by a wide variety of PM emission sources resulting in a complex mixture of aerosols. Furthermore, Colima's air quality is frequently influenced by the volcanic emissions from the Volcan de Fuego de Colima.

As stated above two of the main economic activities performed in the state of Colima are agriculture and cattle breeding. These might emit a wide variety of primary and secondary PM. The indiscriminate use of fertilizers and the frequent occurrence of controlled burning of sugar cane crops performed previously to harvest in the period from October to May highly contribute to increase atmospheric emission of pollutants. In USA regions with high cattle breeding (such as Eastern North Carolina), high concentrations of secondary inorganic aerosols (SIA) related to the conversion of gaseous precursors from farming and the use of animal manure as fertilizers have been found. Thus, in Eastern North Carolina, the mean concentration of SIA (SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>) accounted for 8 µg/m<sup>3</sup> in PM<sub>2.5</sub> (Walter et al., 2006). A strong correlation between NH<sub>4</sub><sup>+</sup> and SO<sub>4</sub><sup>2-</sup> in farming regions has also been determined (Kelly et al., 2005).



**Figure 1.** (a) Map of state Colima, showing the location of the sampling site and the main pollution sources; (b) vegetation types predominating agricultural areas. (a) Thermolectric central and metallurgical industry; (b) mining (Iron ore extraction); (c) sugar industry.

The information on  $PM_{10}$  levels and composition in the Western Mexico is scarce. Galindo et al. (1999) reported high levels of Si, S,  $Cl^-$ , Ca, and Ti, among others. Miranda et al. (2000) identified an association of the elements S,  $Cl^-$ , Cu, and Zn. A recent study by Campos-Ramos et al. (2009) was devoted to the mineralogical characterization of  $PM_{10}$  in the study area by using scanning electron microscopy (SEM). All these studies related the presence of these elements in ambient air to the Volcan de Fuego eruptions.

Further research is needed to interpret the variability of  $PM_{10}$  levels and components and to identify the main emission sources influencing ambient air  $PM_{10}$  levels in order to define cost effective emission abatement strategies. The present study is aimed to collect and integrate data on the levels and composition of rural background of  $PM_{10}$  and to quantify the contribution of the major  $PM_{10}$  sources taking into account the diverse anthropogenic and natural sources localized relatively close to Colima City.

Colima has a warm climate, with an average annual temperature of 25 °C, a mean relative humidity of 65% and an average annual rainfall of 900 mm (INEGI, 2005). Winds from the SW predominate with a frequency of 53%. However, there are some recirculation episodes at the regional level characterized by the effects of SW–NE sea breeze (Galindo et al., 1999) which may favor the transport the particle emissions from sources located in this sector, and the ageing and formation of secondary aerosols by interaction between particulate and gaseous pollutants of different origins. However, since it is located on the western region of the country, is also subject to the influence of anticyclonic systems

generated in the Pacific Ocean. These systems provide a great atmospheric stability, inhibiting the vertical mixing of air.

Among the main pollution sources is the Volcan de Fuego de Colima, located 35 km northeast from the city. This is historically the most active volcano in Mexico and one of the most active ones in Latin America (Galindo et al., 1999). Studies performed in urban and rural areas close to the volcano have found an increase in respiratory illnesses which are associated with the presence of particulate matter within a size between 2.5  $\mu m$  and 10  $\mu m$  (Miranda et al., 2004).

Major anthropogenic emission sources of atmospheric pollutants in the area are depicted in Figure 1A, (a) thermolectric central and metallurgical industry, (b) mining (Iron ore extraction), and (c) sugar industry located southwest, northwest and northeast from CUICA, respectively. All these industrial activities use fuel oil for energy production. It is also important to mention that the majority of the territory has a great abundance of vegetation types, predominating seasonal and irrigated agricultural areas (Figure 1B) and an important factor that favors the presence of secondary inorganic component that have not been evaluated so far.

## 2. Methodology

### 2.1. PM sampling and analysis

The monitoring station is located in the University Center for Environmental Sciences (CUICA, 103°48'10.6" W, 19°12'48.9" N, 500 meter above sea level), 12 km away from the city of Colima

the central region of the state of Colima, western central Mexico, approximately 50 km distant from the Pacific Ocean coast (Figure 1). The station is located in a rural area, away from the direct influence of industrial and traffic emissions.

Sampling was carried out from October 2006 to January 2007 and March to May 2007 at the CUICA rural background site. In order to differentiate the sampling periods these are referred as cold and warm periods respectively. However, given the climate in the area, temperatures are fairly constant in the region, and there is not a clear differentiation as regards for temperature between the two periods, with averages of 23 °C and 78% RH for October 2006 to January 2007 and 27 °C and 74% RH for March to May 2007.

Twenty four hour PM<sub>10</sub> samples were collected by means of high-volume samplers (Tisch Environmental, 68 m<sup>3</sup>/h) on quartz fiber filters (Schleicher and Schuell QF20). During the first period sampling was performed at a ratio of one day out of six; during the second period the frequency of sampling was slightly increased. After discarding a few samples owing to electrical problems, the final number of valid samples was 43, with 25 samples in the cold period and 18 in the warm period.

Filters were stabilized before and after sampling at 23±2 °C and 40±5% relative humidity. Bulk PM<sub>10</sub> concentrations were determined by gravimetry, using standard procedures (NOM–035–SEMARNAT–1993). Thereafter, a fraction of each filter of approximately 150 cm<sup>2</sup> was acid digested (HF:HNO<sub>3</sub>:HClO<sub>4</sub>, with a mixture of 2.5:1.25:1.25 ml, respectively, kept at 90 °C in a Teflon reactor for 6 h, driven to dryness and re-dissolved with 1.25 ml HNO<sub>3</sub> to make up a volume of 25 ml with water) for the chemical analysis using Inductively Coupled Plasma Atomic Emission Spectrometry (ICP–AES, IRIS Advantage TJA Solutions, THERMO) for the determination of the major and some trace elements (Ca, Al, Fe, Mg, Na, K, Ti, Sr and Mn, among others), and Inductively Coupled Plasma Mass Spectrometry (ICP–MS, X Series II, THERMO) for the trace elements (As, Ba, Cd, Cr, Cu, Mn, Ni, Pb, Sb, Se, Sr, Ti, V, and Zn, among others).

For quality control of the analytical procedure a small amount (15 mg) of the NIST–1633b (fly ash) reference material loaded on a similar fraction of blank quartz microfiber filter was also analyzed. Concentrations of major and trace elements are in the range of those usually found at ambient air concentrations. Blank concentrations were subtracted. Analytical errors determined were <10% for most elements, with the exception of P and K (<15%).

Another fraction of filter of about 75 cm<sup>2</sup> water leached with de-ionized water (30 g of Milli-Q grade water) to extract the soluble fraction. The solution obtained was analyzed by ion chromatography for determination of Cl<sup>–</sup>, SO<sub>4</sub><sup>2–</sup>, and NO<sub>3</sub><sup>–</sup>, and by colorimetry – Flow Injection Analysis (FIA) for NH<sub>4</sub><sup>+</sup>.

A third portion of filter of around 1 cm<sup>2</sup> was used to determine total carbon content using a LECO elemental analyser (Querol et al., 2004). SiO<sub>2</sub> and CO<sub>3</sub><sup>2–</sup> were indirectly determined on the basis of empirical factors (SiO<sub>2</sub> = 2.5 × Al<sub>2</sub>O<sub>3</sub> and CO<sub>3</sub><sup>2–</sup> = 1.5 × Ca + 2.5 × Mg) (see Querol et al., 2001). This ratio was previously determined for dust samples collected in Spain and could differ from the actual ratio in Colima, not determined. Sea salt sulfate (SO<sub>4</sub><sup>2–</sup><sub>ss</sub>) concentration was determined from the Na concentration according to the Na/SO<sub>4</sub><sup>2–</sup> molar ratio observed in sea water (Drever, 1982). The difference between total sulfate and marine sulfate is named as non sea salt sulfate (SO<sub>4</sub><sup>2–</sup><sub>nss</sub>). The non mineral carbon (C<sub>nm</sub>) was estimated by subtracting the C associated to the carbonates from the total carbon. Then, OM+EC levels were estimated by applying a factor of 1.6 to the concentrations of C<sub>nm</sub> (Turpin et al., 2003).

PM<sub>10</sub> components were grouped as: crustal material (Σ Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, CO<sub>3</sub>, Ca, Fe, Mg, K), secondary inorganic aerosols (SIA, Σ SO<sub>4</sub><sup>2–</sup><sub>nss</sub>, NO<sub>3</sub><sup>–</sup>, NH<sub>4</sub><sup>+</sup>), sea salt (Σ Na, Cl, SO<sub>4</sub><sup>2–</sup><sub>ss</sub>), and total carbon (C<sub>t</sub>). The percentage of PM<sub>10</sub> mass determined with respect to the total PM<sub>10</sub> mass was >80%, being the rest attributed to water. It should be noted that this determination of percentages is similar to the usually obtained in other areas by using this methodology (75–85%), suggesting that this method is applicable to this area and that SiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ratio used is probably very similar to the local ratio.

## 2.2. Source apportionment analysis

In order to identify different source contributions to ambient PM<sub>10</sub> levels, a Varimax rotated factor analysis (Thurston and Spengler, 1985a) was performed. Factor analysis model aims to describe the input ambient data as a function of source profiles and source contributions, as shown in the equation  $X = G F$ , where X is the concentration matrix for the different components, G is the source contribution matrix, and F is the source profile matrix. Quantification of the source contributions is then performed by multi-linear regression analysis (MLRA), using absolute score factors as source tracers. This methodology is described in depth by Thurston and Spengler (1985b).

Different source apportionment methods have been widely applied for aerosol particulate matter research. A compilation and discussion about application of these methods is provided by Viana et al. (2008). Recently, a special issue on Application of Receptor Models has been published in Air Pollution Research (Hopke and Cohen, 2011).

In this study FA–MLRA was applied with the software package STATISTICA 4.2 to a set of 43 PM<sub>10</sub> samples, using the complete (27 elements) chemical data series of concentrations of PM<sub>10</sub> as independent variables. Number of samples available was relatively low given that a number of samples lower than 50 is not recommended (Henry et al., 1984; Thurston and Spengler, 1985b).

## 2.3. Meteorological analysis

The origin of the air masses affecting the study area during the sampling period was determined by calculating back-trajectories using the NOAA HYSPLIT4 model (Draxler and Rolph, 2003). Five-day back-trajectories were calculated daily at 12:00 GMT, with a 6 h interval. According to the topography of the state of Colima, the starting height of the back-trajectories was set at 500 m a.s.l. According to their origin the following five scenarios were considered: 1) RE: regional episodes with a relatively low dispersion of pollutants; 2) WOP: air masses from the Pacific ocean transported over west Mexico; 3) NUS: air masses from north USA passing through the north of Mexico; 4) EMG: air masses from the Gulf of Mexico transported over the east of the country; 5) PNS southeast air masses from the Caribbean. Additionally, aerosol maps from the Marine Meteorology Division of the Naval Research Laboratory (NAAPS) were employed to identify the episodes with the contribution of anthropogenic material from other zones, mainly from the central portion of the Mexican Republic and the Pacific Ocean.

Data of wild fires occurring during the sampling period were obtained from the CUICA database (Galindo and Dominguez, 2002), and the number of daily exhalations of Volcan de Fuego de Colima was obtained from the register of the Civil Protection State System (<http://www.ucol.mx/volcan/boletines/index.htm>).

### 3. Results and Discussion

#### 3.1. PM<sub>10</sub> levels

Average PM<sub>10</sub> levels determined gravimetrically for the 43 daily samples collected in the study period were 48±16.2 µg/m<sup>3</sup>. PM<sub>10</sub> concentrations were relatively low during the colder period, with average PM<sub>10</sub> levels of 42±17 µg/m<sup>3</sup>, and higher during the warmer period, 56±11 µg/m<sup>3</sup>. Around 50% of the samples exceeded the maximum daily guideline value (50 µg/m<sup>3</sup>) established by the World Health Organization (WHO, 2005). By considering only during the warm period this percentage increases, with around 75% of the sampling days exceeding the 24 h value.

According the HYSPLIT back trajectory analysis, the following type of air masses were identified according their atmospheric transport patterns: RE, Regional; WOP, Western–Ocean Pacific; NEUS, Northeast–United States; EMG, East–Gulf of Mexico; PNS, Peninsula–South. The regional scenario represents low advective conditions with local–regional air mass origin.

As shown in Table 1, during the cold period RE air masses prevailed (40% of days) over WOP and NEUS (28 and 24%), PNS (8%) and EMG (not detected). In the warmer period, NEUS days dominated (39%) over RE and EMG (28 and 22%), PNS (11%) and WOP (not detected). Likewise during NEUS episodes, the transport of the emissions from the northeast sector of the state of Colima, such as those from the Volcan de Fuego and agricultural activities are favored.

As regard to PM<sub>10</sub> recorded for the different episodes, the highest values were obtained for the RE scenarios in the two periods (56 and 59 µg/m<sup>3</sup>), indicating that probably the main source of PM pollution has a local–regional origin. Additionally, these high PM<sub>10</sub> levels may be favored by low–gradient barometric scenario that favors the stagnation of air masses at ground levels and the formation of SIA in the cold period, and by the resuspension of mineral dust from soil in the warm period. During the warm period PM<sub>10</sub> levels were similarly high for all air mass transport scenarios (53–59 µg/m<sup>3</sup>), whereas in the cold period WOP and PNS yielded clearly lower levels (35 and 31 µg/m<sup>3</sup>).

It is important to note that during this study cyclonic systems generated on the Pacific Ocean mainly during the cold period were observed, generating WOP winds that might favor the incoming of tropical marine air with light humidity content. This scenario induces low PM<sub>10</sub> levels in Colima due to scavenging processes caused by an increased rainfall. On the other hand, in the warm period the state is affected by the incoming of warm and humid air from PNS favoring the transport and dust resuspension from the rocky substrate.

Galindo et al. (1998) evidenced the influence of sea breeze in the region caused by the prevalence of south–southwest wind direction in diurnal hours (8:00 to 20:00 h GMT), and north–northeast in nocturnal hours (20:00 to 8:00 h GMT).

#### 3.2. PM<sub>10</sub> speciation

The sum of the concentrations of PM<sub>10</sub> species determined by the previously described methodology accounts, as an average, for 84.5% of the total PM<sub>10</sub> mass, the remaining unaccounted fraction

being attributed to the presence of water molecules in the PM<sub>10</sub> sample and components.

Average, maximum and minimum concentrations of major and trace elements in PM<sub>10</sub> during the sampling period are shown in Table 2 and the distribution of PM<sub>10</sub> components during the two periods is depicted in Figure 2. Below are summarized the levels obtained for the major groups of PM<sub>10</sub> components analyzed.

(1) Mineral matter: The sum of the average concentrations of Mg, K, Fe, Ca, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub> and CO<sub>3</sub><sup>2-</sup> contributes to 32% of PM<sub>10</sub> (15 µg/m<sup>3</sup>), as average for the whole study period, showing a clear seasonal variation. Thus, mean crustal load accounts for 10 µg/m<sup>3</sup> (25% of PM<sub>10</sub>) during the cold period, and for 22 µg/m<sup>3</sup> (39%) during warm period, reaching to daily values of up to 32 µg/m<sup>3</sup>. These values are relatively high when compared with available data from other urban and rural sites in Mexico, (Querol et al., 2008; Vega et al., 2009; Vega et al., 2010), with mean concentration of mineral matter ranging from 10 to 15 µg/m<sup>3</sup>, accounting for 25% of PM<sub>10</sub>. Mineral load is also high when compared with other rural sites, such as Montseny (Spain), with average concentrations of 4 µg/m<sup>3</sup> (24%) in PM<sub>10</sub> (Pey et al., 2009).

The high crustal contributions measured, especially in the warm period, may be due to enhanced resuspension of soil and industrial dusts and volcanic ash and to the higher emission of silicate particles from agricultural fires (Campos et al., 2009). It is worthy to note that due to the high crustal load, K in PM<sub>10</sub> is mostly associated to feldspars and clay minerals (illite), and not with biomass burning. This is supported by the high K/Al correlation (R<sup>2</sup>=0.8) and the low K intercept in the regression equation. Actually, a fraction of Na should also be attributed to the mineral component given de high Na/Al correlation (R<sup>2</sup>=0.6).

(2) The secondary inorganic aerosols (SIA, sum of the concentrations of SO<sub>4</sub><sup>2-</sup><sub>nss</sub>, NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> account for 30 and 21% of PM<sub>10</sub> for the cold and warm periods, respectively, showing very similar concentrations at the two periods (12.5 and 11.6 µgSIA/m<sup>3</sup>). Average concentrations for the whole period for specific components were 9.3, 2.1 and 1.0 µg/m<sup>3</sup>, for SO<sub>4</sub><sup>2-</sup><sub>nss</sub>, NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>, respectively (Table 3). The concentrations of SO<sub>4</sub><sup>2-</sup><sub>nss</sub> may be considered as high if compared with usual concentrations measured at other sites in Mexico, ranging from 3–6 µg/m<sup>3</sup> (Querol et al., 2008; Vega et al., 2009; Vega et al., 2010). By contrast levels of nitrate are relatively low (3–6 µg/m<sup>3</sup>). As shown in Figure 3 there is not a clear seasonal variation for SIA components. Thus, average concentrations of NH<sub>4</sub><sup>+</sup> were similar in the cold and warm periods (2 µg/m<sup>3</sup>), showing daily peaks of up to 6 µg/m<sup>3</sup> in the October–November 2006, and January 2007 simultaneously with high levels of sulfate. Levels of nitrate are slightly higher in the warm period, with peaks of up to 6 µg/m<sup>3</sup> usually recorded during wild fire episodes. By contrast, levels of sulfate are relatively higher in the cold period, showing a more marked variability with daily levels reaching to values up to 19 µg/m<sup>3</sup>. As shown in Figure 3, the sulfate peaks are not always related to the volcanic and fire episodes. Origin of these high levels of sulfate may be related to meso–scale air mass transport or emissions from anthropogenic sources at regional and or local scales.

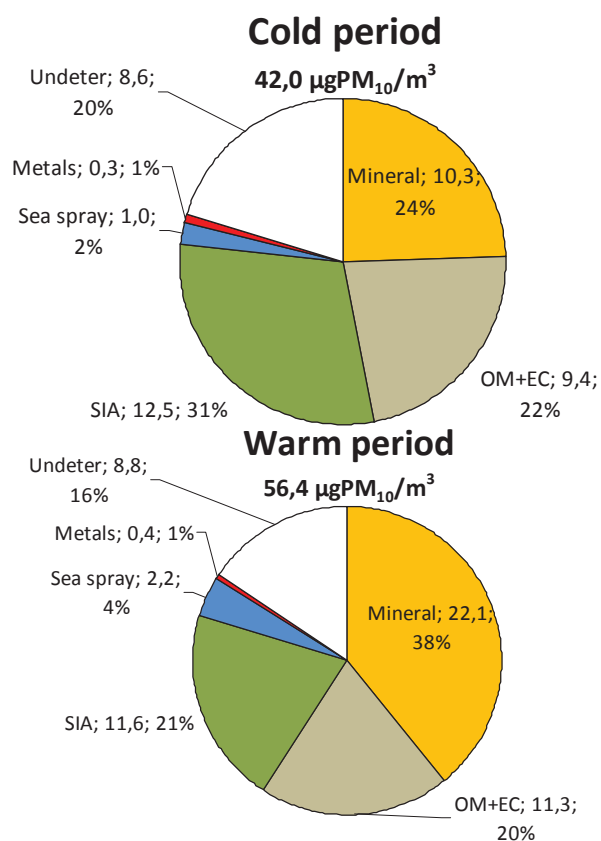
**Table 1.** Frequency of air mass transport scenarios and mean PM<sub>10</sub> levels recorded for each of these episodes during the cold and warm periods at CUICA station (RE: Regional, WOP: Western–Ocean Pacific, NEUS: Northeast–United States, EMG: East–Gulf of Mexico, PNS: Peninsula–South)

	Cold Period					Warm Period				
	RE	WOP	NEUS	EMG	PNS	RE	WOP	NEUS	EMG	PNS
Frequency (%)	40	28	24	ND	8	28	ND	39	22	11
PM <sub>10</sub> (µg/m <sup>3</sup> )	56	35	46	ND	31	59	ND	53	56	56

ND: Not detected

**Table 2.** Average, maximum and minimum concentrations of major and trace elements in PM<sub>10</sub> during the sampling period (October 2006 to May 2007) at the monitoring station CUICA

N = 43	Average	Max	Min		Average	Max	Min
	(μg/m <sup>3</sup> )				(ng/m <sup>3</sup> )		
PM <sub>10</sub>	48.0 ± 16.2	78.5	14.9	P	74.8 ± 32.5	184.3	24.6
OM+EC	10.2 ± 3.1	16.4	2.7	Ti	70.3 ± 41.5	159.6	11.1
Al <sub>2</sub> O <sub>3</sub>	2.6 ± 1.6	5.9	0.4	V	36.5 ± 28.2	126.6	6.2
SiO <sub>2</sub>	7.9 ± 4.8	17.8	1.3	Zn	29.8 ± 21.6	106.0	4.5
CO <sub>3</sub> <sup>2-</sup>	1.8 ± 1.1	6.6	0.2	Cu	25.7 ± 59.3	398.0	4.0
Ca	1.2 ± 0.7	4.4	0.2	Ba	21.6 ± 30.4	116.0	0.2
Fe	0.8 ± 0.4	1.6	0.2	Mn	18.4 ± 10.1	37.0	3.7
K	0.5 ± 0.3	1.2	0.1	Sr	8.8 ± 4.6	18.2	1.7
Mg	0.3 ± 0.2	0.7	<0.1	Ni	7.1 ± 5.6	31.1	1.0
Na	0.9 ± 0.5	2.2	0.2	Pb	4.2 ± 3.3	14.8	1.2
SO <sub>4</sub> <sup>2-</sup> <sub>ss</sub>	0.2 ± 0.1	0.5	0.1	Cr	1.4 ± 1.5	7.5	0.3
SO <sub>4</sub> <sup>2-</sup> <sub>nss</sub>	9.0 ± 4.1	19.1	3.4	As	1.1 ± 2.3	15.8	0.3
NO <sub>3</sub> <sup>-</sup>	1.0 ± 1.0	5.9	0.1	Sb	0.9 ± 0.5	2.7	0.3
Cl <sup>-</sup>	0.4 ± 0.3	1.2	<0.1	Cd	0.2 ± 0.2	0.9	0.1
NH <sub>4</sub> <sup>+</sup>	2.0 ± 14	6.8	0.2	Se	0.4 ± 0.3	1.4	0.1
				Mo	2.4 ± 1.6	5.3	0.3

**Figure 2.** Composition of PM<sub>10</sub> the CUICA station in the warm and cold periods.**Table 3.** Number of events of volcanic exhalations and fires observed around the CUICA station

Month/year	Volcanic exhalations	Fires
November/06	3	UR
January/07	23	UR
March/07	12	2
April/07	UR	8
May/07	5	20

UR: Unrecorded

Given the low concentrations of nitrate, ammonium is usually related to sulfate, with a clear excess of sulfate, deducing the presence of partially neutralized ammonium sulfate. When considering all the daily samples, correlation of sulfate and ammonium is  $R^2=0.42$  (Figure 4a); if concurrent samples with volcanic exhalations are discarded, the correlation increases up to  $R^2=0.78$  (Figure 4b). Then, it is evidenced that during volcanic eruptions there is an important contribution of sulfur compounds to the atmosphere in the study area. Campos et al. (2009) identified by SEM the presence of barium sulfate particles, which were attributed to volcanic emissions. Nevertheless, the presence of sulfuric acid particles formed from oxidation of SO<sub>2</sub> volcanic exhalations should be considered.

(3) Sea salt was calculated as the sum of Na<sup>+</sup>, Cl<sup>-</sup> and SO<sub>4</sub><sup>2-</sup><sub>ss</sub> with an average concentration for the whole period of 1.5 μg/m<sup>3</sup> (3.2% of PM<sub>10</sub>). A relatively high concentration was observed in the warm period (2.2 μg/m<sup>3</sup>), probably due to effect of enhanced sea breeze circulations pattern (Galindo et al., 1999). This sea salt contribution must be considered as the maximum possible contribution given the low correlation determined between the levels of Na and those of Cl<sup>-</sup>. This low correlation may be partially attributed to the interaction between NaCl aerosols and nitric phases (Harrison and Pio, 1983), resulting in the depletion of Cl<sup>-</sup>. Nevertheless, given the high correlation between Na and Al ( $R^2=0.6$ ), it is deduced the existence of a fraction of crustal sodium, usually present in feldspars, such as albite, in addition to the marine one. Moreover, presence of Cl<sup>-</sup> may be related to emissions of agricultural fires (Murindi et al., 2004; Hays et al., 2005).

(4) Organic matter and elemental carbon (OM+EC), calculated from non mineral carbon, accounts for 21% of PM<sub>10</sub> (10 μg/m<sup>3</sup>) showing a low variation along the study period, with a slightly higher concentration during the warm period (11 μg/m<sup>3</sup>). In the study area carbonaceous aerosols may be emitted by a variety of sources such as road traffic or sugar cane burning episodes, more frequent from November to March after the harvest. In addition to these primary sources the formation of secondary organic aerosols should also be considered, that is probably enhanced during the warmer period.

(5) Trace elements: The contribution of trace elements was similar in the two periods (0.3 and 0.4 μg/m<sup>3</sup>). The elements with elevated average concentration (> 20 ng/m<sup>3</sup>) were P, Ti, V, Zn, Cu and Ba. Low levels of As, Sb and Cd were measured, although the level of most trace elements are relatively high when compared with other rural background PM<sub>10</sub> data using a similar methodology, for example Montseny, Spain (Pey et al., 2009) and Chaumont, Switzerland (Hueglin et al., 2005). Furthermore, levels of Ni and V are relatively high when compared with urban zones such as Mexico City (Querol et al., 2008, by using a similar methodology), Barcelona Metropolitan area (Querol et al., 2001) and Tocopilla, Chile (Jorquera, 2009). This differential pattern may arise from the widespread combustion of fuel-oil in the state of Colima.

### 3.3. Source apportionment

It is important to note that the number of possible factors from Principal Component Analysis are limited by the variance of the original elements. The analysis yielded to the identification of the factors below that accounted for a cumulative variance of 82% (Table 4).

**Factor 1.** This factor refers to “regional sources” (45% of the variance) and it is composed of crustal material resuspended soil dust and volcanic ashes (Fe, Ti, Al, Si), agricultural dust and the occurrence of forest fires (OM+EC, K, P, Sr, Fe, NO<sub>3</sub><sup>-</sup>). Previous studies on the characterization of PM emission sources from Colima state (Campos-Ramos et al., 2009), reported that Fe, Ti and

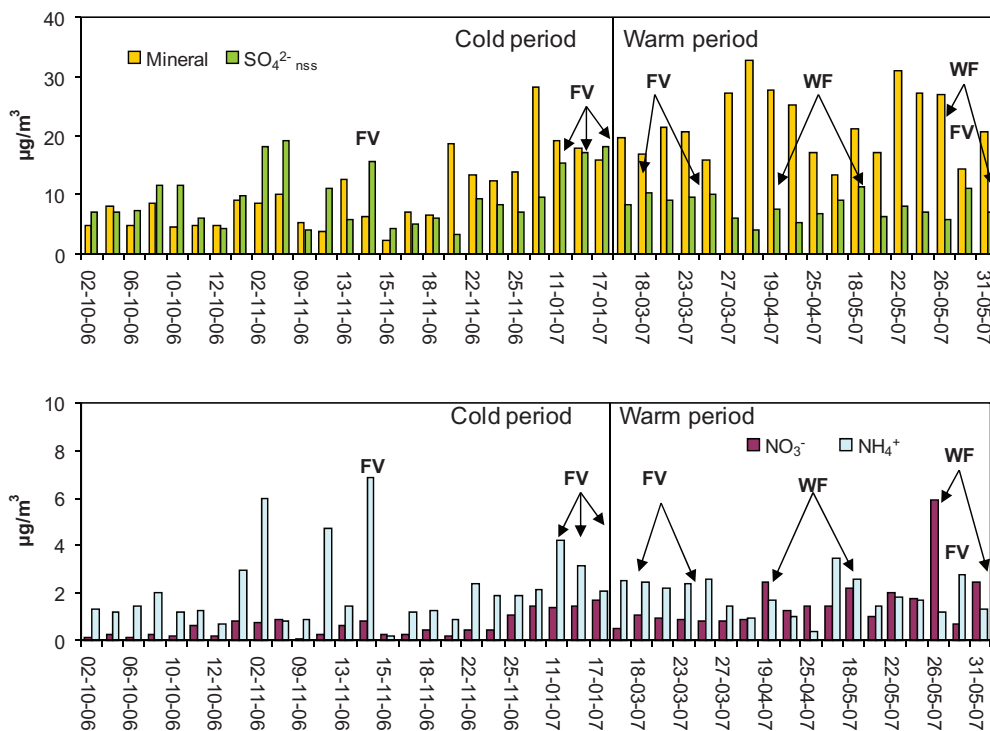


Figure 3. Levels of SIA ( $SO_4^{2-nss}$ ,  $NH_4^+$ ,  $Cl^-$  and  $NO_3^-$ ) in  $PM_{10}$  for the cold and warm periods. Episodes simultaneous with Volcan de Fuego exhalations (FV) and wild fires (WF) indicated.

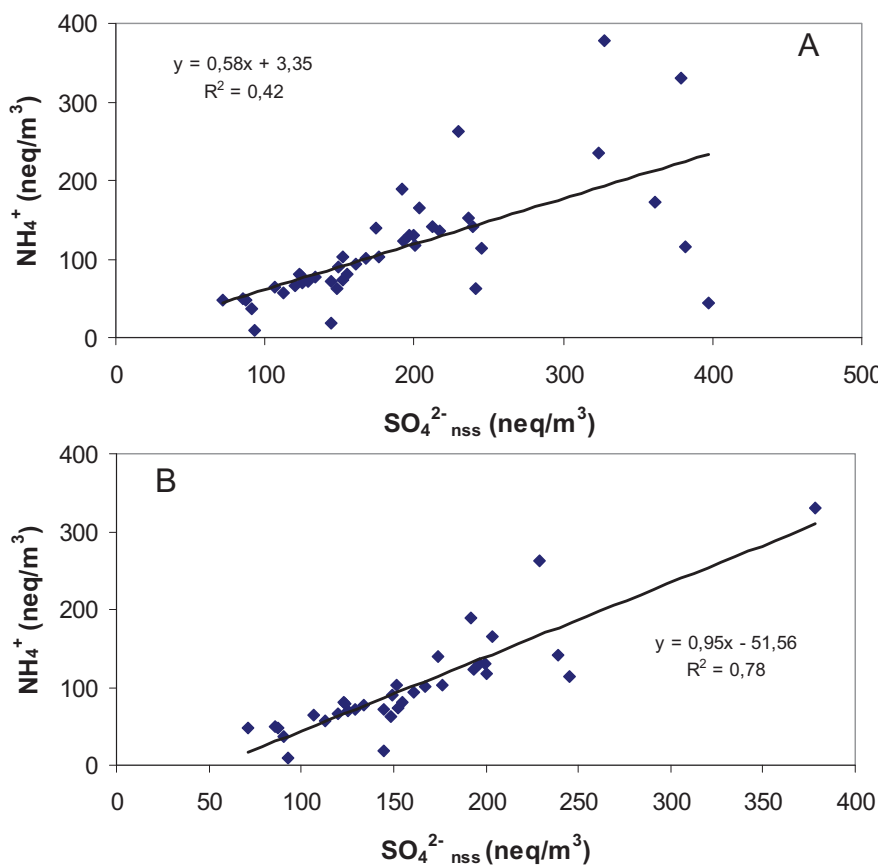


Figure 4. Correlation between levels of  $SO_4^{2-nss}$  and  $NH_4^+$  (in  $neq/m^3$ ) by considering all the samples (a) and discarding samples simultaneous with volcanic episodes (b).

**Table 4.** Results of the factor analysis carried out with the daily concentrations of  $PM_{10}$  components. Weightings for each factor after Varimax normalization

	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
$PM_{10}$	<b>0.81</b>	0.16	0.33	0.26	-0.15
OM+EC	<b>0.70</b>	0.16	0.16	0.40	0.12
Al	<b>0.97</b>	0.03	0.00	0.09	0.08
Ca	0.56	<b>0.73</b>	-0.11	0.22	0.15
Fe	<b>0.90</b>	0.27	0.05	0.24	0.02
K	<b>0.92</b>	-0.08	0.14	0.06	0.14
Mg	<b>0.99</b>	0.06	0.03	-0.05	-0.04
Na	<b>0.87</b>	-0.01	0.03	-0.10	-0.30
Ba	0.29	0.32	0.36	0.66	0.06
Cu	-0.07	<b>0.94</b>	-0.03	0.19	0.03
Mn	<b>0.86</b>	0.40	0.04	0.24	0.05
P	<b>0.92</b>	-0.05	-0.04	0.09	0.07
Sr	<b>0.91</b>	0.27	-0.01	0.23	0.06
V	0.09	-0.08	<b>0.91</b>	-0.14	-0.15
As	-0.07	<b>0.95</b>	-0.03	0.22	0.00
Se	0.18	0.52	-0.01	0.43	0.01
Cd	0.27	<b>0.71</b>	0.20	0.48	-0.13
Pb	0.10	0.22	-0.11	<b>0.71</b>	-0.22
Ti	<b>0.96</b>	0.14	-0.01	0.11	0.07
Ni	0.14	0.08	<b>0.91</b>	0.11	-0.04
Zn	0.07	0.26	0.23	<b>0.83</b>	0.12
Sb	0.16	0.28	-0.12	<b>0.75</b>	-0.05
Zr	0.62	-0.18	0.03	0.33	0.02
$SO_4^{2-ss}$	<b>0.87</b>	0.00	0.02	-0.09	-0.30
$SO_4^{2-nss}$	-0.05	-0.10	<b>0.71</b>	0.23	<b>-0.53</b>
$NO_3^-$	<b>0.67</b>	0.04	0.07	0.10	0.01
$Cl^-$	0.57	0.26	0.26	-0.38	0.07
$NH_4^+$	-0.01	-0.01	0.30	0.06	<b>-0.84</b>
Expl.Va	11.34	3.93	2.76	3.54	1.39
Prp.Tot	0.40	0.14	0.10	0.13	0.05
EigenV	12.69	4.64	3.05	1.57	1.01
Total	45.32	16.57	10.90	5.60	3.61
Source	Regional	Industrial	Fuel-oil	Road	Secondary

K, Na, Si, Al, O rich particles were related to the ilmenite and feldspar discrete particles, from volcanic ash, but these components are also typical from other crustal material, such as dust. Furthermore, carbonaceous Si, Al, Fe rich particles from burning of cultivation of cane were also frequently identified. Sodium was also present in this factor with a lesser contribution. It is important to mention that  $Cl^-$  was not present in this factor. This may be caused by the possible crustal origin (Na–feldspars) of mot bulk (soluble + insoluble) Na or by the mixed source contribution (marine, volcanic and biomass burning) of  $Cl^-$  (Taran et al., 2002).

**Factor 2.** This factor contains metal and metalloid elements, such as Cu, As, Cd, Ca and Se (17% of the variance) typically related to anthropogenic emissions from thermoelectric and metal–metallurgical processes. The transport of such emissions to the study area is favored mainly by the southwestern winds in winter and spring periods. There are no major industrial estates emitting these elements nearby the monitoring station, so their presence is related to the transport at the regional level favored by the incoming air masses from the Pacific Ocean, but also a major volcanic origin could not be discarded.

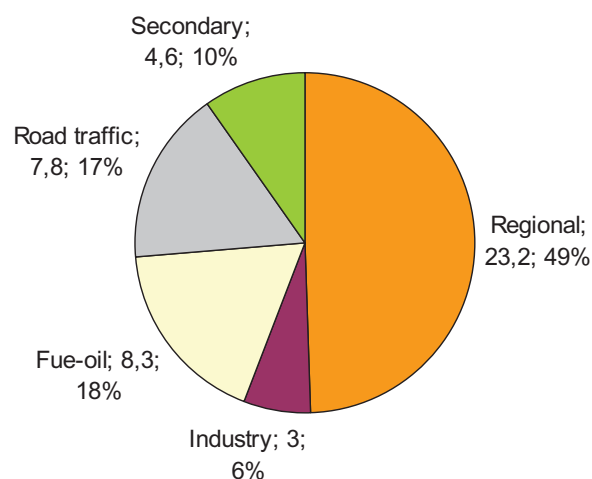
**Factor 3.** This factor is constituted by Ni, V and non sea salt  $SO_4^{2-}$  (11% of the variance), related to widespread fuel–oil combustion at regional level in diverse industries, such as mining, sugar cane processing, metallurgy and power generation.

**Factor 4.** This factor is constituted mainly by Pb, Zn, Ba, Sb and OM+EC (6% of the variance). These PM components are tracers of primary road traffic emissions (Schauer et al., 2006), probably related to a freeway with continuous transit of vehicles is located at 200 m from the monitoring site.

**Factor 5.** Represents the formation of secondary sulfate favored by transport at the regional level. This is constituted mainly by  $NH_4^+$  and non sea salt  $SO_4^{2-}$  (4% of the variance). The major occurrence of  $(NH_4)_2SO_4$  was deduced during the entire sampling period by means of ion balances. The origin of this component is related to the high  $SO_2$  concentrations from sporadic volcanic exhalations, fossil fuel combustion and industrial emissions; and high potential  $NH_3$  from intense agricultural and farming activities.

After identifying the main particulate matter emission sources affecting the sampling area, their mass contributions were determined based on a multiple linear regression analysis. The modeled and experimental results for  $PM_{10}$  levels showed a very good fit, with  $R^2$  of 0.90.

Figure 5 shows that the average regional contribution accounts for 49% of the  $PM_{10}$  mass ( $23 \mu g/m^3$ ) owing to the high contribution of crustal material. The contribution of the industry reached to 6% of the  $PM_{10}$  mass ( $3 \mu g/m^3$ ). Additionally, both fuel–oil combustion and road traffic contribute each with  $8 \mu g/m^3$ , accounting for 17–18% of the  $PM_{10}$  mass. Finally, the contribution of secondary sulfate is 10% of the  $PM_{10}$  mass ( $5 \mu g/m^3$ ).



**Figure 5.** Average contribution of  $PM_{10}$  from main emission sources determined by PCA: regional, industrial, fuel–oil, road traffic and secondary sulfate formation.

#### 4. Conclusions

The present study allowed the measurement and interpretation of the variability of  $PM_{10}$  and its different components in a rural background site (CUICA) at Colima, Mexico. Average  $PM_{10}$  levels reached to relatively high values ( $48 \mu g/m^3$ ). Relatively high levels of crustal material ( $15 \mu g/m^3$ ) carbonaceous aerosols ( $10 \mu g/m^3$ ) and sulfate ( $9 \mu g/m^3$ ) account for the increased  $PM_{10}$  levels for a rural background site.

Dust resuspension, volcanic, industrial, agricultural, farming and road traffic emissions, as well as regional pollution were identified as the main drivers of this variability. Furthermore, meteorological factors at local, regional and synoptic scales influenced such  $PM_{10}$  variability.

A differentiation was found between the cold period, with average  $PM_{10}$  levels reaching to  $42 \mu g/m^3$ , and the warm period, with  $56 \mu g/m^3$ . The first study period was characterized by high levels of  $SO_4^{2-nss}$  ( $19 \mu g/m^3$ ) arising from both anthropogenic and

volcanic emissions, whereas the second is characterized by a high contribution from crustal material ( $22 \mu\text{g}/\text{m}^3$ ) from soil resuspension and volcanic ash.

The occurrence of most trace elements (Pb, As, Cu, Zn, Cd, V, Ni, Cr, Sb,) arise from regional and long distance transport of diverse anthropogenic emissions. The elements with relatively high levels when compared with other rural, urban and industrial areas were Ni and V. The source apportionment analysis showed that the highest contribution to  $\text{PM}_{10}$  levels arises from the regional pollution (49 %) followed by the industrial emissions, fuel oil combustion, road traffic and secondary sulfate (18, 17, 10 and 6%, respectively).

The results from the present study show a large anthropogenic load in rural background PM pollution, consequently, we propose to build an air quality monitoring network in rural and urban areas of this region.

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