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Fine Particles Composition and Emission Chemical Profiles from Sugarcane Production for Source Reconciliation Applying the Chemical Mass Balance

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Abstract. Every year, many tons of fine particles are emitted to the atmosphere due to the sugarcane-mills operation and for inadequate agricultural practices such as sugarcane burning. In order to foster a deeper knowledge about the levels and source contributions of particles and their toxic species, the City of Cordoba was selected for two $PM_{2.5}$ sampling campaigns to be carried out in the center and in a rural location at 9 km far, during harvesting and non-harvesting seasons; additionally, the chemical source profiles from sugarcane burning and sugar mills were determined. The $PM_{2.5}$ levels in the City of Córdoba ranged from 29.9 to 102.1 $\mu g\ m^{-3}$ and from 13 to 36.6 $\mu g\ m^{-3}$ in the harvest and non-harvest periods, respectively, but toxic chemical species rose up to nine times representing an important risk health. Total carbon concentrations during harvesting were around 67 % and 64 %. With the chemical source profiles and the $PM_{2.5}$ airborne concentrations, the Chemical Mass Balance Model was applied for source reconciliation, evincing that sugarcane processes accounted with 22 % of fine particles, vehicles with 34 to 38 %, secondary inorganic aerosols from 16 to 24 %, and suspended particles from roads from 10 to 20 %. The results show that inhabitants in this area are exposed to high levels of $PM_{2.5}$ in harvesting, with a high risk to their health. This study provides valuable information to the authorities for the $PM_{2.5}$ control strategies design and protect the population health, during harvesting.
Keywords: $PM_{2.5}$; sugarcane; biomass burning; CMB model; source profiles.

Resumen. Cada año, se emiten muchas toneladas de partículas finas a la atmósfera debido a la operación de los ingenios azucareros y a prácticas agrícolas inadecuadas como la quema de caña de azúcar. Con el fin de fomentar un conocimiento más profundo sobre los niveles y las contribuciones de origen de las partículas y sus especies tóxicas, la ciudad de Córdoba fue seleccionada para llevar a cabo dos campañas de muestreo de $PM_{2.5}$ en el centro y en una ubicación rural a 9 km de distancia, durante las temporadas de cosecha y no cosecha; además, se determinaron los perfiles químicos de la quema de caña de azúcar e de los ingenios. Los niveles de $PM_{2.5}$ en la ciudad de Córdoba oscilaron entre 29.9 y 102.1 $\mu g\ m^{-3}$ y entre 13 y 36.6 $\mu g\ m^{-3}$ en los períodos de cosecha y no cosecha, respectivamente, pero las especies químicas tóxicas se incrementaron hasta nueve veces, lo que representa un importante riesgo a la salud. Las concentraciones totales de carbono durante la cosecha fueron aproximadamente del 67 % y el 64 %. Con los perfiles químicos de origen y las concentraciones de $PM_{2.5}$ en el aire, se aplicó el Modelo de Balance de Masas Químicas para la reconciliación de fuentes, demostrando que los procesos de caña de azúcar representaban el 22 % de las partículas finas, los vehículos el 34 al 38 %, los aerosoles secundarios del 16 al 24 %, y las partículas suspendidas de las carreteras del 10 al 20 %. Los resultados muestran que los habitantes de esta zona están expuestos a niveles altos de $PM_{2.5}$ durante la cosecha, con un alto riesgo para su salud. Este estudio proporciona información valiosa a las autoridades para el diseño de estrategias de control de $PM_{2.5}$ y proteger la salud de la población, durante la cosecha.

Palabras clave: $PM_{2.5}$; caña de azúcar; quema de biomasa; modelo CMB; perfiles de fuentes.

Introduction

Sugarcane is cultivated in tropical countries and represents a significant economic impact for the agroindustry of the producing countries that yield sugar and ethanol [1].

More than half of the sugarcane harvest worldwide is done manually, involving the crop burning to remove foliage, snakes and venomous insects; after harvesting, mostly straw and residues are also burned for land preparing and pests control [2,3].

This agricultural practice annually generates tons of pollutant particles that have adverse effects on the health of people living in sugarcane-growing areas, causing and exacerbating cardiorespiratory diseases [4,5]. Hospital admissions for asthma crises, respiratory diseases, hypertension, and long-term kidney problems, particularly among harvesters, increase during harvesting periods [6,7]. Atmospheric fine particles are able to damage living organisms due to their so small sizes that can penetrate very deep into the lungs, but also due to their composition, since some elements, such as metals, can generate free radicals or reactive oxygen species (ROS) capable of inducing oxidative stress in the cells [8]; moreover, organic compounds like some polycyclic aromatic hydrocarbons (PAH) in particles are immunosuppressants and have mutagenic and carcinogenic properties [9]. In addition, particles resulting from incomplete biomass burning contain black carbon in soot, which is a short-lived climate pollutant (SLCP) that increases the greenhouse effect, contributing to global warming and climate change [10,11].

In Mexico, sugar production generates around 450,000 direct jobs and brings indirect benefits to more than 2.2 million people. Veracruz contributes with 40 % of national production [12]. More than 80 % of the harvest is done manually with pre-burning harvest between November and May [13]. Although Mexico has an air quality standard for respirable and fine particles (PM_{10} and $PM_{2.5}$), monitoring is only performed in cities with more than 500,000 inhabitants. Therefore, all the sugarcane-growing areas with fewer inhabitants have very little information on air pollution and lack timely notifications to protect themselves against particle concentration levels and their toxic contents, which can be very high during harvesting as was reported in the sugarcane areas of Morelos and Chiapas, where $PM_{2.5}$ concentrations were up two folds higher during harvesting and toxics, such as polycyclic aromatic hydrocarbons levels rose 2 to 6 times in that period [14,15].

During the harvesting period, the primary sources of particle emissions, which enclose a great number of inorganic and organic compounds and elemental carbon are believed to originate predominantly from sugar mills and agricultural burning, although the contribution from vehicles on freeways and trucks transporting sugarcane from fields to mills is also significant [11]. It has been reported that during harvest the visits to hospitals are increased due to the exacerbation of cardiorespiratory illness [16], moreover, some compounds included in the airborne particles from sugarcane burning and sugar-mills possess carcinogenic and mutagenic activity, representing a health risk for the population [17]. Recently, a comprehensive study reported that exposure to the ashes from sugarcane burning can lead to respiratory, cardiovascular, and renal health issues and that studies related to the ashes chemical characterization and funding are needed to understand the damage and toxicological mechanisms on people [18]. Given these multifaceted factors, it is imperative for environmental authorities to discern the relative $PM_{2.5}$ contributions of sugarcane processes and other sources to effectively safeguard public health. Mass balance receptor models have been developed to address this need, facilitating the identification and quantification of particle sources; among them, the Chemical Mass Balance model (CMB) has proven to be particularly valuable in delineating particle sources from individually collected samples, because it is possible the quantification of every source contribution in individual samples, differing of other multivariate analyses, as the Principal Component Analysis that only generates a qualitative diagnostic or the positive matrix factorization which requires a large number of analyzed samples [19,20,21]. In the context of sugarcane-growing regions specifically, Afshar-Mohajer *et al.* [22] conducted a study quantifying the contribution of several sources to the presence of polycyclic aromatic hydrocarbons, thereby shedding light on the complex dynamics of air pollution in these areas, however, there is a lack of information related to the composition of $PM_{2.5}$, their inorganic species and the origin of them. Against this backdrop and guided by the evidences that toxic species concentrations present in particles escalate during harvesting, this study was undertaken for over a year to characterize the chemical composition of atmospheric particles with the objective to ascertain the concentrations of $PM_{2.5}$ and PM_{10} and associated toxics to which people residing in the most significant sugarcane-producing area are exposed. Additionally, $PM_{2.5}$ chemical source profiles were determined for both, sugar mills and sugarcane burning, enabling the estimation of sources contribution to the presence of $PM_{2.5}$ and its chemical species in the city center of Cordoba and a rural area located 9 km far using the CMB model.

Experimental

Sampling sites

The Cordoba municipality is a medium city of the Veracruz State with around 200,000 inhabitants of which 45.7 % are men and 54.3 % women [23]. It is located at 860 m above sea level (18° 53'N; 96° 56'W) and is surrounded by eight sugar mills and hundreds of hectares of sugarcane crops, which are burned every year during harvesting emitting hundreds of particulate matter (PM) tons which can cause adverse effects in the exposed population, especially in agriculture workers (17 %) followed by the children up to 10 years old which constitute around 24 % and the 16 % of vulnerable population of adults over 60 years [23]. The sampling campaigns were carried out during the sugarcane harvesting and no-harvesting seasons from January 2015 to November 2016, but the sampling began four months before in the rural site, since in the downtown a special permission was required. The Municipal Palace (MP) in the Cordoba downtown was the first site for the particles monitoring, whereas a rural zone, 9 km far from the city and located in the Postgraduate College (PC), was the second sampling site. $PM_{2.5}$ Hi Vol samplers (Tisch Environment), with conditioned Whatman quartz fiber filters, were used to collect 24 h integrated samples each two weeks (Fig.1).

In the rural site PC, was installed also a PM_{10} Hi Vol sampler, in order to know the $PM_{2.5}$ fraction related to PM_{10}, since in this location there are many sugarcane crops and an intense agricultural activity. After collection, filters were wrapped with foil and stored at 4 °C before gravimetry and chemical analyses. The meteorological parameters were registered in the station of the Veracruz University.

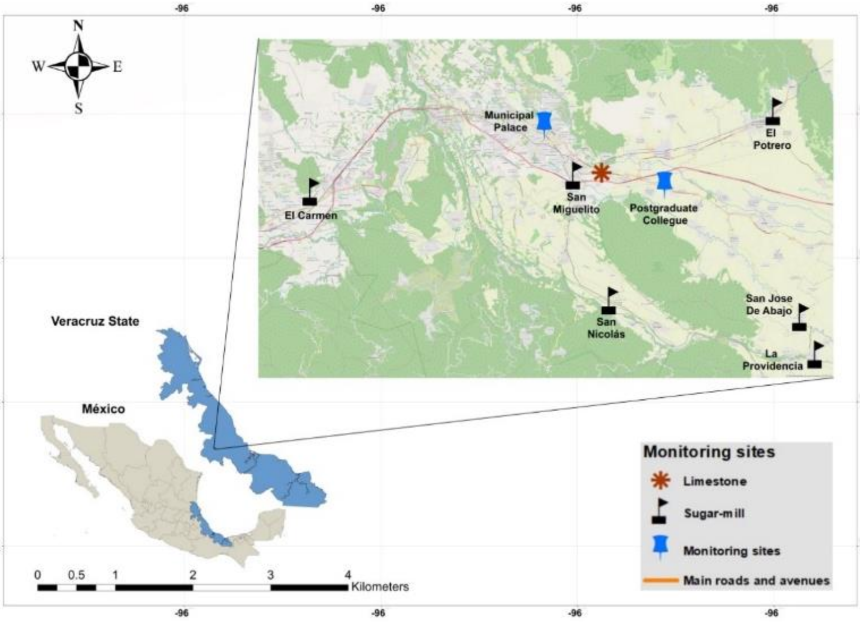

Fig. 1. Location of sampling sites Municipal Palace (MP) and Postgraduate College (PC) and sugarcane-mills.

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Chemical source profiles

For the development of the $PM_{2.5}$ chemical profile of sugarcane-mills, a sampling campaign of one week was performed at 200 m downwind from one sugar mill, when the sugarcane harvest had finished and there were no more burnings; whereas the $PM_{2.5}$ chemical profile from crop burnings was carried out sampling at one km downwind from the sugar fields during five burning practices, at the beginning of the harvesting season when sugar mills activity was starting.

Chemical analyses

Organic and elemental carbon analyses were performed in duplicate in an Optical Carbon Aerosol Analyzer with reflectance correction (Sunset Lab, Forest Grove, OR USA), to measure the organic (OC) and elemental carbon (EC) concentrations, according with the NIOSH-5040 method described by Birch and Cary [24].

PAH were extracted ultrasonically with dichloromethane (Bransonic), during three times for 10 min periods at 10 °C and concentrated in a rotary evaporator for further quantification analysis with a chromatograph (GC model HP 6890) coupled with a mass spectrometer using a 30 m HP5-MS capillary column (0.25 mm ID, 0.25 μm film thickness).

For the ion analyses, a soluble fraction was extracted with Milli-Q deionized water in an ultrasonic bath (Branson bath, 3210) during 15 min for further evaporation at 60 ºC. Samples were filtered, and the ammonia ion was quantified with an NH_4^+ selective electrode and a Thermo ORION STAR potentiometer. Other ions were analyzed twice by HPLC chromatography (Jasco LC-NetII/ADC) with a BioLC ED50 electrochemical detector (Dionix) and a IC-Pak Anion HR, 75x4.6 mm column (Waters).

The elemental analysis was carried out by digestion of 35 cm^2 of the filter with nitric acid and perchloric acid in a Savillex Teflon, leading to dryness and rebuilding with a diluted acid solution. The solution was analyzed through an inductively-coupled plasma atomic emission spectrometer ICP-AES for major elements and with ICP-MS for trace elements (Thermo X series). SiO_2 and CO_3^{2-} were indirectly determined based in stoichiometric relationships.

Chemical Mass Balance Model

The Chemical Mass Balance (CMB) receptor model use multivariate analysis to estimate particles and chemical species source contributions based on the degree to which source profiles can be combined to reproduce ambient concentrations[19,25]; the CMB model requires as input data the chemical receptor concentrations, the source profile chemical composition obtained in this study and in previous researches as well as data uncertainties to estimate the source contributions for the $PM_{2.5}$ total mass and finally the standard errors of those estimations. The CMB8.2 software was used for the estimations [19]. The fundamental equation of receptor model (equation 1) is derived from the mass conservation equation and represents the relationship between the concentration of aerosol measured at the receptor and that emitted by the sources.

$$Ci = \sum_{j=1}^{J} Fij * Sj \tag{1}$$

where:

Ci = Concentration of “i” pollutant measured
Fij = Fraction emitted of “i” pollutant by the source “j”
Sj = Calculated contribution of “j” source
J = Number of contributing sources

Environmental data obtained from sample characterization were combined with chemical profiles derived from sugarcane burning and mill emissions developed in this study. Additionally, source profiles of light-duty and diesel vehicles, were included [26]. Agricultural soils paved and unpaved roads, and limestone processes from previous studies were profiles also utilized [27]. Moreover, source profiles from industrial facilities available in the Speciate database [28] were incorporated into the analysis.

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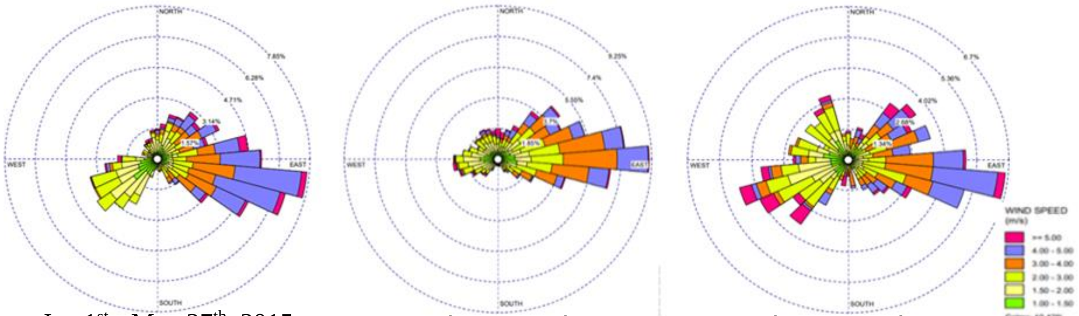
Quality assurance

Prior to sampling, quartz filters underwent calcination at 600 °C for 4 hours to eliminate any adsorbed organic matter. Flow calibration procedures were conducted before sampling during each season. Following calcination, the filters were stored in a controlled environment for 48 hours at a constant temperature of 25 ± 5 °C and relative humidity of 45 % ± 5 % before being weighed using an analytical balance. To validate elemental analysis, standard urban dust reference material (SRM 1649a) was utilized adding 20 mg to a 4 cm^2 blank filter to determine the analysis accuracy, following the same handling and analysis procedure as the filters and blanks. The performance of the CMB model was assessed based on the recovery mass percentage and various statistical parameters R^2 and Chi^2, blank filter to check the accuracy of the analysis.

Results

Fine particles and carbonaceous compound concentrations

The meteorological conditions prevailing in the 3 sampling periods: harvesting (January 1st to May 27th 2015), non-harvesting (May 30th to November 20th), and harvesting (February 5th to March 5th), are presented in the rose winds of Fig. 2, where it is possible to observe that the dominant winds originated from the east in the first harvest period and in the non-harvest period, while in the second harvest period there was also a significant influence of west winds, although with lower speed. This means that most of the year the emissions from the rural zone are transported to the center; however, in the latter part of the harvest period, there was a noticeable influence of westward winds, albeit at a reduced velocity.



Jan 1st - May 27th, 2015 May 30th - Nov 20th, 2015 Feb 5th - March 5th, 2016

Fig. 2. Wind speed and direction during sampling campaigns.

The time series of $PM_{2.5}$ concentrations in the downtown area (MP) and at the rural site (PC), alongside the PM_{10} concentrations at the PC is illustrated in Fig. 3. The PM_{10} concentrations at the PC ranged from 44 to 147 µg m^{-3} during harvesting, with the air quality maximum permissible limit exceeded on 7 days of 35 samples. The $PM_{2.5}/PM_{10}$ ratio varied from 64 to 71 %, indicating a predominance of fine particles over coarse ones. During the harvesting season, $PM_{2.5}$ concentrations at both sites were two times higher than those during non-harvesting periods, highlighting the significant impact of various sugarcane processes on air pollution. Furthermore, $PM_{2.5}$ concentrations in the downtown area (MP) were consistently 15 % to 40 % higher than those recorded at the rural site, indicating a notable contribution from vehicular and commercial activities. $PM_{2.5}$ mass concentrations ranged from 34 to 102 µg m^{-3} in the city and from 27 to 90 µg m^{-3} at the rural site during harvesting. Statistical analysis using the Mann-Whitney test revealed significant differences between sampling periods and locations (P value ≤ 0.05). Throughout the harvesting season, the $PM_{2.5}$ Mexican air quality standard of 45 µg m^{-3} (NOM-025-SSA1-2014) was exceeded 18 times at the MP site out of 22 samples (16 with very poor air quality and 2 with poor air quality), while at the PC site, there were 14 exceedances in 35 samples (7 with very poor air quality and 7 with poor air quality). Conversely, during the non-harvesting season, the air

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quality standard was not exceeded at either site. However, the USEPA standard of 35 µg m^{-3} was surpassed on 40 % of days. These results show the necessity of major supervision in the sugarcane-mills emission, as well as the reduction of biomass burning.

Although the concentrations during the harvest period were lower than those observed in Morelos state, close to the Zacatepec sugar mill, they were higher than those reported in Chiapas [14], while the PM_{10} concentrations during harvesting were similar to those reported by de Andrade *et al.* [17], who shows the mutagenic activity of atmospheric particles emitted during the harvest season. Several authors have reported an increase in hospital admissions due to high pollution levels reached during the harvesting season, resulting in exacerbations of asthma, various respiratory diseases, and aggravation of cardiovascular problems in various cities in Brazil [16,29]. In addition, studies in Brazil and Mexico reported an increase in diseases, whereas several deaths have been associated to sugarcane burning in South Florida [30]; then, avoiding preharvest burning undertaking green cane harvest, would represent an improvement in health [31].

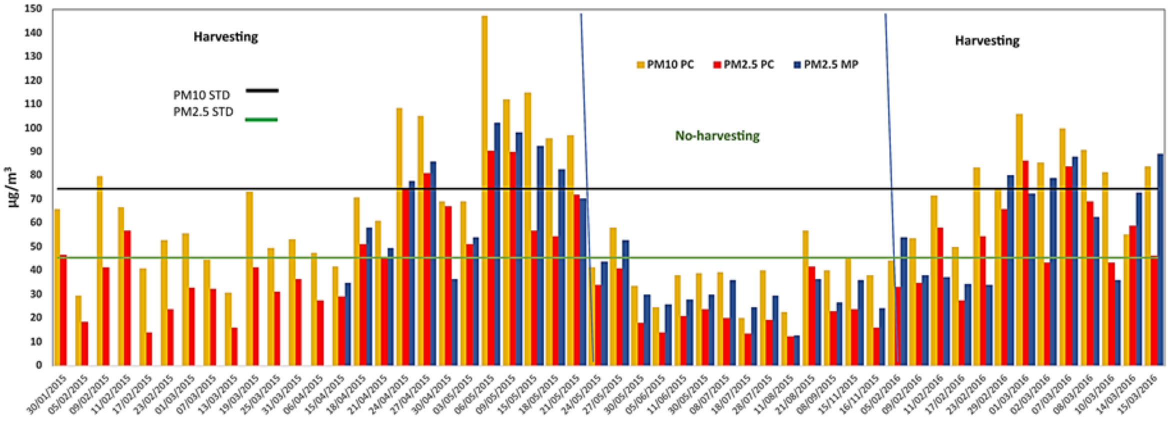
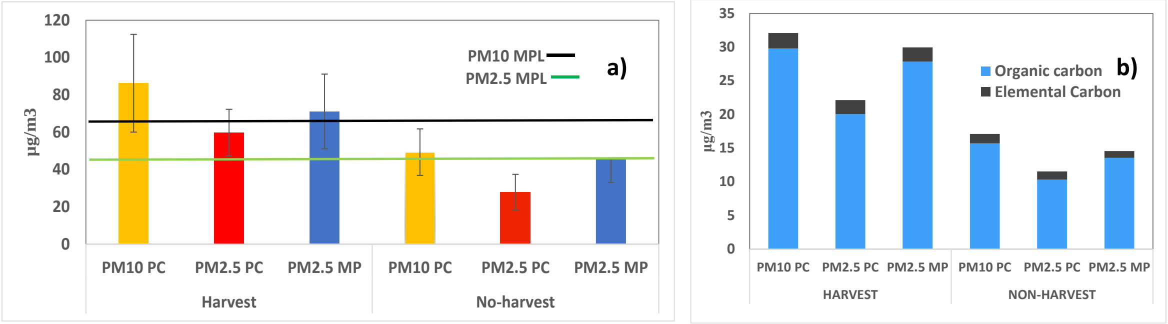


Fig. 3. Time series of $PM_{2.5}$ and PM_{10} concentrations in Cordoba, Veracruz.

Fig. 4 presents the averages of $PM_{2.5}$ and PM_{10} concentrations, alongside the average concentrations of total carbon (TC) contained within the particles, which constitutes the most abundant species formed by the sum of organic and elemental carbon (OC + EC). The TC average concentrations were around two times higher in harvesting than in non-harvesting (23 vs 10 µg m^{-3}, respectively). The OC/TC ratio ranged from 0.87 to 0.92 in both particle sizes, which is higher to the studies performed in Mexico City in 1997 and 2009, with a ratio of 0.73 and 0.76 with TC concentrations average of 15.8 and 15.4 µg m^{-3}, respectively [32,21]. Other characterization studies performed in rural zones in Europe reported lower $PM_{2.5}$ and TC concentrations than this study in the non-harvest season [33], in opposite, the $PM_{2.5}$ concentrations in rural zones in Chine are at least twice than those found in this study, with concentrations of 115 µg m^{-3} and 24 µg m^{-3} of TC, which are alike to those found in non-harvest season [34]. The greater TC concentration in $PM_{2.5}$ at MP compared to the TC concentrations in PM_{10} and $PM_{2.5}$ suggests the contribution of organic carbon from urban sources such as restaurants and intense vehicular traffic, among others. The high TC concentration in the sugarcane zone indicates a low combustion efficiency in the processes occurring in the sugarcane processing, whereas the significant contribution of sugarcane burning, and sugarcane mills is confirmed by observing that TC decreases by a third during the non-harvest season; of especial mention is the 60 % increasing of EC in harvest, since this is a climatic forcer and has been proposed that the ban of sugarcane burning could reduce the 7 % of total black carbon in Mexico [11], this measure, besides to be a mitigation action for climate change would have co-benefices in the air quality improvement.



MPL Maximum permissible limit

Fig. 4. (a) Average PM_{10} and $PM_{2.5}$ concentrations and **(b)** average concentration of carbon species.

Polycyclic aromatic hydrocarbons in $PM_{2.5}$

PAH are compounds characterized by two or more fused aromatic rings, typically formed during the pyrolysis or incomplete combustion of organic matter, leading to soot formation [14]; although these compounds, contained in the organic carbon fraction of $PM_{2.5}$ were not used into the Chemical Mass Balance for source apportionment, due to the absence of source profiles for this compound family, 17 PAH recommended by the USEPA, were measured and characterized owing to their pronounced toxicity. The quantified PAH encompassed a range of compounds including: naphthalene (NAP), methylnaphthalene (MNAP), acenaphthylene (ACY), acenaphthene (ACE), anthracene (ANT), phenanthrene (PHE), benzo[a]pyrene (BAP), benzo[b]fluoranthene (BBF), benzo[a]anthracene (BAA), fluorene (FLU), fluoranthene (FLT), pyrene (PYR), chrysene (CRY), benzo[k]fluoranthene (BKF), 2-methylnaphthalene (MNAP), dibenzo[a,h]anthracene (DBA), indene[1,2,3-cd]pyrene (IND), and benzo[ghi]perylene (BGP). Despite $PM_{2.5}$ and organic carbon exhibited higher concentrations in the city in comparison to the rural zone, Fig. 5 reveals that during harvesting, the highest concentrations of PAH were observed in the rural site, which is in close proximity to and surrounded by sugarcane fields that were eventually burned. Conversely, the city is situated farther away from biomass burning sites; although, during the non-harvesting period, most PAH exhibited higher concentrations in the city (MP), underscoring the significance of local sources. The sum of PAH were 5.3 and 2.9 ng m^{-3} in PC and PM, respectively in the harvest time, and individual PAH were 2 to 7 times greater than during the no-harvest period, primarily due to crop burning, emissions from sugar mills, and diesel emissions from numerous trucks queuing to unload harvested sugarcane, these results are in agreement with a study reported in Brazil [17] where concentrations were five times greater in harvest than in non-harvest. It is common during harvesting to observe soot particles suspended in the air or deposited on the ground. In non-harvest season the sum of PAH were 1.1 and 1.5 ng m^{-3} in PC and PM, showing the contribution of traffic and other combustion sources in the downtown. Of particular concern is the contribution of carcinogenic compounds to the PAH mixture, accounting for 57-58 % and 59-61 % during the harvest and non-harvest periods, respectively.

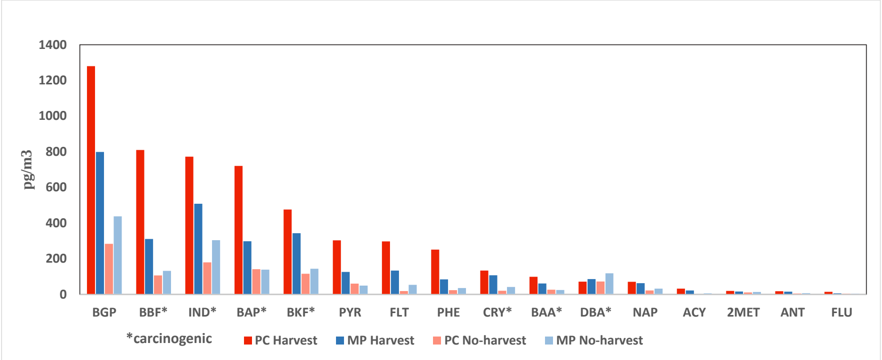


Fig. 5. Polycyclic aromatic hydrocarbons concentrations in harvesting and no-harvesting periods.

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The assessment of carcinogenic potential involves the sum of the concentration of each individual PAH multiplied by its toxic equivalent factors which were proposed by Nisbet and Lagoy [35] to determine the benzo[a]pyrene equivalent concentration (BAP_{eq}). The relative individual contribution of cancer risk and the BAP_{eq} during the harvest season in the rural site of Cordoba is presented in Table 1, where is possible to observe that BAP_{eq} increased three times in MP and two times in PC and the individual PAH increase from 2 to 7 times such as BBF. Although the annual BAP_{eq} averages in PC and PM were lower with 641 and 419 pg m^{-3} respectively, than the annual PM_{10} European Union and WHO [36] recommendation of 1000 pg m^{-3} for health protection, they exceeded the annual PAH limit of the United Kingdom of 250 pg m^{-3} and France of 100 pg m^{-3} [37]; furthermore, inhabitants are exposed to high levels of PAHs during six continuous months in the harvest period, with significant health impacts associated to sugarcane processes.

Table 1. Carcinogenic potential (BAPeq) of the Polycyclic Aromatic Hydrocarbon in $PM_{2.5}$.

	BAPeq [pg/m^3]				
Compound	**TEF**	**Harvesting**		**No-harvesting**	
	Toxic Equivalency Factor	**MP $PM_{2.5}$ urban**	**PC $PM_{2.5}$ rural**	**MP $PM_{2.5}$ urban**	**PC $PM_{2.5}$ rural**
Naphtalene	0.001	0.07	0.063	0.032	0.022
2-Methylnaphtalene	0.001	0.019	0.015	0.013	0.011
Acenaphtylene	0.001	0.032	0.022	0.005	0
Acenaphtene	0.001	0	0	0	0
Fluorene	0.001	0.014	0.005	0.004	0.003
Phenanthrene	0.001	0.251	0.084	0.036	0.023
Anthracene	0.01	0.18	0.15	0.07	0.05
Fluoranthene	0.001	0.297	0.133	0.053	0.018
Pyrene	0.001	0.303	0.126	0.049	0.06
Benzo [a] anthracene	0.1	9.9	6.1	2.4	2.6
Chrysene	0.01	1.33	1.07	0.41	0.2
Benzo[b]fluoranthene	0.1	81	31.1	13.2	10.6
Benzo[k+j]fluoranthene	0.1	47.6	34.3	14.4	11.6
Benzo[a]pyrene	1	720	298	139	141
Indene[1,2,3-cd]pyrene	0.1	77.3	50.9	30.4	18
Dibenzo[a,h]anthracene	1	71	86	118	72
Benzo [g,h,i] perylene	0.01	12.8	7.99	4.38	2.83
Total Benzo[a]pyrene eq		**1022**	**516**	**322**	**259**

The PAH increase in sugarcane pre-harvest burning has been documented in studies conducted in Brazil, United States, and Mexico, as well as PAH levels increase in several urban sites in the winter season; a comparison among several studies is presented in Table 2; due to the lack of data, some comparisons were made with PAH in PM$_{10}$. The carcinogenic potency as BAP$_{eq}$ is a good parameter for comparison among different studies since they are directly obtained from PAH individual concentrations and the TEFs.

Table 2. Comparison of PAH levels and BAPeq (carcinogenic potency) from biomass burning with other studies.

Site	**PM µg/m³**	**Σ PAH ng/m³**	**BAP ng/m³**	**BAP eq ng/m³**	**Reference**
Cuernavaca, Morelos, México PM$_{2.5}$	-	25.4-22.5	2.6-2.2	-	**Saldarriaga *et al.*, 2015[38]**
Zacatepec, Morelos México harvest PM10	72-203	3.9-5.8	0.46	1.014	Mugica *et al.* 2015[14]
Araraquara, Brazil harvest PM10	76-182	11.6	0.5		de Andrade *et al.*, 2012[17]
Araraquara, Brazil harvest PM10	29-41	14.1 ± 13	0.26		de Assunsao, *et al.* 2014[39]
Sao Paolo, sugarcane belt				0.13-3	Scaramboni *et al.*, 2024[40]
Mexico City PM10	52-164	0.7-17.8	0.04-1.4	0.41-2.18	Mugica *et al.*, 2010[41]
North, China	57.7 ± 37	15.3 ± 8.8	1.5 ± 1.2	-	Wang *et al.*, 2018[42]
Tehran, Iran	32.1 ± 17	12.2 ± 7	0.23 ± 0.17	29 ± 5.7	Taghvaee *et al.*, 2018[43]
Venice, Italy	32.2 ± 25	9.8 ± 12.5	1.2 ± 1.8	1.9 ± 2.6	Masiol *et al.*, 2012[44]
Thessaloniki Greek	36 ± 19	9.4 ± 9.3	0.7 ± 0.8	0.85 ± 0.4	Manoli *et al.*, 2016[45]
Florence, Italy	13.6-29.6	13-3.6	0.2-1	0.79-3.3	Martellini *et al.*, 2012[46]
Changzhou, China	28.9-308	235.29	24.5	41.1	Bi *et al.*, 2020[47]
PC Harvest	44.3 ± 19	5.3 ± 2.6	0.7 ± 0.4	1.02	This study
PC No Harvest	20 ± 8.4	1 ± 0.2	0.1 ± 0.08	0.25	This study
MP Harvest	62.4 ± 23	2.9 ± 0.8	0.2 ± 0.1	0.5	This study
MP No Harvest	28.1 ± 8	1.5 ± 0.4	0.1 ± 0.05	0.32	This study

Bold: studies in harvest season

The ΣPAH in this study during harvesting are similar to that reported in the sugarcane zone of Zacatepec, México, as well as the estimated BAP$_{eq}$ that is into the range of that reported in the Sao Paolo sugarcane belt; but ΣPAH are lower than the values reported in two studies in Araraquara, Brazil during harvest, in the cities of Cuernavaca, Mexico, Theran, Venice, Florence, Changzhou and Thessaloniki, showing that PAH have usually higher total mass and carcinogenic potency in cities than in rural sites. Quite high values in the cities of Iran and China are explained for the high traffic of diesel vehicles as well as by industrial activities.

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Elemental composition of $PM_{2.5}$

The $PM_{2.5}$ characterization is detailed in Table 3, presenting average concentrations of chemical species identified and quantified in the 57 samples analyzed during both, harvesting and non-harvesting periods. The rise of individual concentrations in harvest is evident in almost all the species. Toxics elements concentrations such as Cu, Pb and Cd increased 9, 2 and 3 times in the Cordoba center. A Kruskal-Wallis test was conducted on all data, revealing significant differences between the two seasons at both sites (P value < 0.05). In general, higher concentrations of the major species were quantified during harvest.

Table 3. Concentrations of chemical species in $PM_{2.5}$ samples and developed source profiles.

	Municipal Palace (MP)				**Postgraduate College (PC)**				**Source profiles**			
Period	**Harvest**		**Non-harvest**		**Harvest**		**Non-harvest**		**Sugarcane-mill**		**Crops burning**	
	Mean	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**
$\mu g\ m^{-3}$												
PM_{10}	-	-	-	-	86.2	26.2	49.3	12.5				
$PM_{2.5}$	71.1	19.98	45.39	7.29	59.77	19.32	27.88	9.54	73.6	25.6	85.49	21.8
TC	30.85	6.35	15.35	3.27	22.85	5.67	11.63	3.3	19.14	5.91	26.3	6.37
OC	27.85	5.92	13.55	3.05	20.04	5.07	10.32	2.7	16.99	4.22	19.73	4.55
EC	3	0.53	1.8	0.22	2.81	0.74	1.31	0.8	2.15	0.47	6.58	0.69
SiO_2	1.7	0.39	0.74	0.14	2.1	1.78	0.66	0.02	7.66	0.27	1.81	0.62
Al_2O_3	0.39	0.16	0.30	0.06	0.72	0.71	0.04	0.01	1.62	0.09	0.38	0.11
Cl^-	0.13	0.08	0.08	0.1	0.12	0.06	0.07	0.2	0.05	0.03	0.08	0.04
NO_3^-	0.47	0.24	0.99	0.10	0.91	0.59	0.23	0.14	0.72	0.21	0.11	0.08
SO_4^{2-}	9.01	1.94	6.87	1.36	8.86	4.49	2.78	2.94	1.98	1.54	2.85	1.72
NH_4^+	3.98	0.95	1.92	0.25	2.21	1.11	0.61	0.45	0.27	0.73	1.87	0.64
Na	0.07	0.03	0.09	0.04	0.71	0.31	0.23	0.18	6.35	0.05	0.01	0.01
K	0.98	0.143	0.58	0.31	0.68	0.35	0.23	0.21	0.7	0.32	17.23	2.76
Mg	0.06	0.02	Bdl	0.16	0.09	0.07	0.01	0.01	1.29	1.1	0.16	0.06
Al	0.19	0.10	0.23	0.11	0.38	0.38	0.2	0.09	1.62	0.97	0.38	0.18
P	0.04	0.02	0.06	0.05	0.05	0.03	0.02	0.01	0.52	0.41	0.075	0.06
Ca	0.37	0.05	1.21	1.00	0.54	0.39	0.13	0.2	3.89	1.92	0.34	0.26
Ti	0.02	0.01	0.00	0.02	0.02	0.02	0.01	0.02	0.09	0.06	Bdl	Bdl
Fe	0.24	0.07	0.29	0.14	0.24	0.23	0.05	0.02	0.41	0.13	0.07	0.04

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	Municipal Palace (MP)				**Postgraduate College (PC)**				**Source profiles**			
Period	**Harvest**		**Non-harvest**		**Harvest**		**Non-harvest**		**Sugarcane-mill**		**Crops burning**	
	Mean	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**	**Mean**	**SD**
ng m^{-3}												
Li	0.17	0.05	0.08	0.00	0.15	0.08	0.01	0.01	0.87	0.54	Bdl	Bdl
Be	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	Bdl	0.03	0.02	Bdl	Bdl
Sc	0.01	0.00	0.01	0.01	0.01	Bdl	Bdl	Bdl	0.04	0.02	Bdl	Bdl
V	3.58	0.59	2.36	0.69	4.12	4.80	1.24	0.54	2.23	1.53	0.91	0.62
Cr	0.06	0.01	0.05	0.00	0.25	0.44	0.06	0.01	4.64	1.97	Bdl	Bdl
Mn	12.69	2.82	4.61	1.47	13.13	12.16	2.59	1.1	11.86	3.25	2.95	1.15
Co	0.10	0.03	0.04	0.07	0.12	0.09	0.04	0.01	0.27	0.17	0.32	0.14
Ni	2.00	0.85	0.90	0.27	2.79	2.94	0.007	Bdl	0.71	0.41	2.08	0.99
Cu	149.8	74.84	16.09	3.27	22.90	11.17	16.6	12.3	24.87	14.8	4.89	2.58
Zn	106.5	26.24	38.21	Bdl	45.94	21.77	32.8	17.5	70.14	29.8	14.47	9.36
As	0.53	0.10	0.81	Bdl	0.40	0.15	0.17	0.1	1.11	0.09	1.08	0.85
Se	0.16	0.18	0.13	0.06	0.25	0.19	0.063	0.02	0.47	0.23	Bdl	Bdl
Rb	2.00	0.31	0.99	0.08	1.79	0.79	0.80	0.21	1.91	1.1	0.81	0.53
Sr	1.50	0.31	0.71	0.08	2.91	2.68	0.03	0.01	7.89	5.32	2.2	0.98
Y	0.01	Bdl	0.01	Bdl	0.01	Bdl	0.005	Bdl	0.05	0.02	Bdl	Bdl
Zr	5.12	0.56	0.15	Bdl	3.85	2.39	3	0.92	4.04	2.26	4.99	2.33
Nb	0.08	0.04	0.03	0.02	0.07	0.05	0.04	0.01	0.05	0.03	0.05	0.03
Cd	0.35	0.07	0.09	Bdl	0.26	0.14	0.13	0.02	0.11	0.07	0.32	0.18
Sn	4.50	1.20	0.73	Bdl	3.27	2.86	1.4	0.57	0.64	0.42	1.72	1.2
Sb	1.28	0.27	1.66	0.43	1.28	0.56	0.48	0.21	1.58	0.89	0.86	0.63
Cs	0.04	0.04	Bdl	Bdl	0.05	0.05	Bdl	Bdl	0.14	0.07	0.1	0.05
Ba	13.39	5.60	24.12	0.00	12.99	8.86	3	1.1	28.31	9.43	Bdl	Bdl
Tl	0.08	0.01	0.01	0.01	0.09	0.07	0.01	0.01	0.03	0.01	0.17	0.13
Pb	15.22	6.30	7.27	3.66	14.65	7.62	5.55	3.23	2.07	1.03	3.81	2.26
Bi	0.06	0.04	0.01	0.04	0.04	0.04	0.01	Bdl	0.14	0.1	Bdl	Bdl

Th	0.01	Bdl	0.01	Bdl	0.01	Bdl	0.01	Bdl	0.08	0.04	Bdl	Bdl
U	0.01	Bdl	0.01	Bdl	0.01	Bdl	0.01	Bdl	Bdl	Bdl	Bdl	Bdl

Bdl: below detection limit

Although the concentrations of trace elements may appear similar in the examined cases, these small differences are used by the model for multivariate analysis with the source profiles, allowing the estimation of their contributions, for instance, the $PM_{2.5}$ inorganic composition of this study is quite different from $PM_{2.5}$ compositions in Mexico City [21,48]. Notable disparities emerged between the two profiles, establishing each as a distinct fingerprint; the profile associated with sugarcane-mills exhibits elevated levels of metals such as Ca, Mn, Cu, Cr, V, and Sr in the emissions, whereas the biomass burning profile reveals the characteristic presence of potassium. Fig. 6 illustrates the $PM_{2.5}$ mass reconstruction in each site at the two seasons. The most abundant components were the carbonaceous species composed by elemental carbon (EC) and organic matter (OM), which was estimated with OC multiplied by the factor of 1.8 for the hydrogen and oxygen accounting of an average molecular weight of the organic compounds [49].

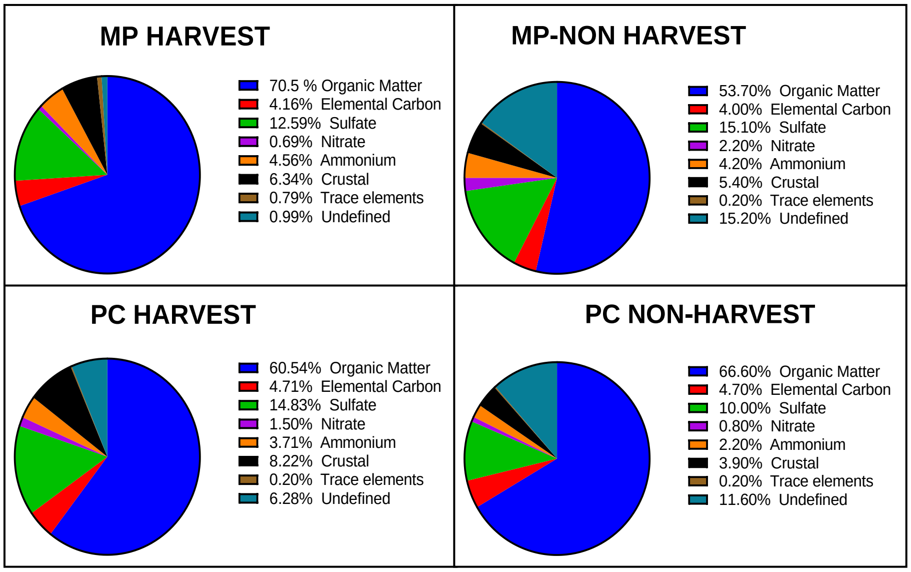

Fig. 6. Composition of $PM_{2.5}$ in harvest and non-harvest in the urban and rural sites.

The OM contribution in the urban site during harvest was 24 % higher than in non-harvest due to the combined effect of sugarcane processes and the activities of the city; while in the rural site the OM influence was higher in non-harvest, because is an agricultural zone with additional crops than sugarcane, which are planted and harvested throughout the year, in addition to livestock and poultry farming in the area.

The second abundant component were the secondary aerosols composed by the $(NH_4)_2SO_4$ and NH_4NO_3, which are formed in the atmosphere when the SO_4^{2-} and NO_3^- ions react with the NH_3 gas emitted by the organic matter decomposition, this component is estimated by the stochiometric relations ($[SO_4^{2-}]$x1.375 and $[NO_3^-]$x 1.29.The $(NH_4)_2SO_4$ was the major contributor in all cases, due to the use of diesel in vehicles and in the processes of the mills and other factories and that the presence of nitrate was low in general.

The geological or crustal component was estimated with the sum of the metal oxides, calculated for each oxide with its stochiometric relationship (Al_2O_3 = Al x1.89; Fe_2O_3 = [Fe] x1.43; CaO = [Ca] x 1.4; K_2O = [K] x 1.2; MgO = [Mg] x 1.66; Na_2O = [Na] x 2.7; TiO_2 = [Ti] x 1.67; P_2O_6 = [P] x 2.29; and the SiO_2 = Al_2O_3 x 2.5) [50]. The crustal fraction in particles was similar in both seasons in the city, meaning that were generated

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locally, but for the rural site the crustal component was twice in harvest than in non-harvest, which implies that transportation in the rural area during the harvest season caused the suspension of a large amount of soil particles. Except for particles composition from the urban site in harvest with around 1 % contribution, the trace metals accounted for 0.2 % of $PM_{2.5}$ total mass.

Source reconciliation with the CMB model application

To the best of our knowledge, the chemical mass balance model had not previously been applied for source attribution using elemental composition profiles in sugarcane areas, although it had been applied for the case of PAH [50]. The CMB model successfully identified 9 sources during the harvest and up to 6 in no-harvest. Table 4 shows the source contribution ranges during the two periods at the urban and rural sites, whereas Fig. 7 presents the average source contributions solved by the CMB model in the 62 samples analyzed. It is possible to observe that the source chemical profiles developed in this study constitute two new chemical signatures which were recognized in the CMB model for differentiate and separate the emissions of the sugar-mills operation from the sugarcane burning emissions as well as from the other used profiles.

Table 4. Source contribution of $PM_{2.5}$ in the urban and rural sites and CMB model performance.

	MP harvesting	**PC harvesting**	**MP non-harvesting**	**PC Non-harvesting**
Source				
Particles from roads	9.9-15.5	6.8-17.5	18.2-22.3	17-30.7
Agricultural soil	5.2-6.1	4.7-21.9	5.8-7.4	6-14.9
Limestone plant	0-5	1.5-11	5.4-7.5	5.4-7.5
Gasoline vehicles	11 a 36	6.8-34	25-30.7	25-30.7
Diesel vehicles	11 a 21	12.4-21.4	13.4-20.5	13.4-20.5
Secondary aerosols	14-24	15-21.7	13.9-23.3	9.7-14.9
Other factories	0	1-8	0	0
Sugar mill	3 a 29.2	3-17.8	0	0
Biomass burning	5 a 21	2-18-2	0	0
Performance				
R^2	0.96±0.03	0.95±0.03	0.93±0.02	0.98±0.01
Ch^2	3.9±1.03	3.6±1.02	3.6±0.7	3.4±1.3
Measured/Calculated	1.1±0.06	0.97±0.04	1.02±0.02	0.96±0.02

The parameters fell within acceptable ranges, indicating the robust performance of the CMB model. The coefficient of determination (R^2) values averaged between 0.97 and 1, while the Chi^2 values were close to 4, and the ratio of measured to estimated mass averaged 1.01. The contribution to the presence of $PM_{2.5}$ in the atmosphere from sugarcane burning combined with the operation of the sugar mill was approximately 22 %, with a greater contribution of emissions from sugarcane mills in the downtown area, as dominant winds transport emissions from surrounding mills; meanwhile, sugarcane field burning contributes similarly in both sites. The most significant contribution is attributed to vehicular activity, as a freeway passes close to the PC site and an interstate highway is located 2 miles away from both sites. During harvesting, in addition to these roads, there are significant diesel vehicular $PM_{2.5}$ emissions from the many old trucks transporting harvested sugarcane to the sugar mills. The total vehicular contribution ranged between 34 and 38 %, with similar levels at both sites; during non-harvesting periods, gasoline vehicles accounted for more than 30 % and diesel vehicles for 27 % in the MP site, as it is also impacted by traffic from numerous streets. This suggests vehicular regulation measures, especially in the renovation of trucks. As was mentioned before, secondary aerosols are important contributors to the fine suspended particles, due to the high temperatures and combustion emissions that favors their formation.

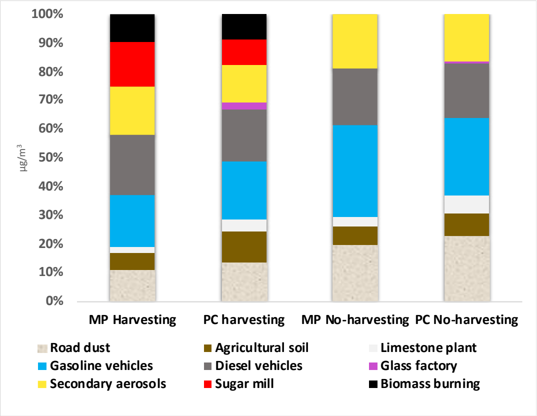

Fig. 7. Source reconciliation of $PM_{2.5}$ in the sugarcane zone in Cordoba, Veracruz.

The emissions from agricultural soils are caused by wind and soil cleaning and preparation for cultivation; therefore, the highest contribution was in the rural area (PC), where most crops are located, with 11 % and 8 % during harvesting and non-harvesting periods, respectively. Vehicle traffic on paved and unpaved roads also has a significant contribution ranging between 11 % and 23 % across different sites and seasons. A limestone facility is located between the two sites, a little closer to the PC that is in operation the whole year. Nevertheless, the contribution of this source is not only from the plant, since limestone is applied in order to neutralize the soil with pH from 4.5 to 5.5. Different blends of $CaCO_3$ and CO are applied onto the sugarcane stalks post-harvest, acting as a nutrient booster for the mother plant, facilitating better absorption of nitrogen, phosphorus, and potassium. This practice is performed for the soil preparation of other crops as well. Consequently, the impact of this source is more pronounced in the rural site during the non-harvesting season, where the majority of crops are cultivated, contributing to over 6 % of the total $PM_{2.5}$ mass. Even during the harvesting season, this source remains relevant as lime application typically commences in December, following the clearing of soil from the initial sugarcane harvesting.

Conclusions

The detailed chemical analysis of the elements and compounds that comprise fine atmospheric particles suspended in the air, known as $PM_{2.5}$, not only provides a diagnosis of the presence of toxic species for living organisms but can also be used in receptor models to determine the contribution of various emitting sources.

This study demonstrates that during the sugarcane harvest season, $PM_{2.5}$ concentrations were duplicated, exceeding the maximum permissible limits of the Mexican standard on 70 % of days, resulting in poor or very poor air quality. The 60 % increase in elemental carbon or black carbon during harvesting presents

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an opportunity for achieving co-benefits in climate change mitigation and air quality improvement through decision-makers' actions.

The successful generation of chemical source profiles for the two main sugarcane processes, was achieved for the first time, because the source signatures were able to differentiate and separate emissions from mills and burnings, which had not been previously published, as well as to identify the contribution from the 2 to 5 % lime application in the field to neutralize the soil. During the harvest, mills contribute to $PM_{2.5}$ emissions between 9 and 15 %, while biomass burning contributes around 9 %, vehicles contribute 36 % on average, and road dust and agricultural soil contribute from 18 to 22 %.

Of special concern is the increase in toxic species in particles, which can be up to 9 times higher compared to the non-harvest season. In particular, some carcinogenic polycyclic aromatic compounds were up to 7 times higher, and some inorganic toxics increased their concentration up to 9 times, mainly in urban areas where the population density is higher. This diagnosis should be used by environmental and health authorities to reinforce the need for control measures, in both, mills and in crop fields. Additionally, these results underscore the importance of conducting health risk assessments in the area.

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