Black Carbon and Particulate Organic Toxics Emitted by Sugarcane Burning in Veracruz, México

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Abstract—Sugar cane industry signifies a very important income for the Mexican economy; nevertheless, the inadequate agricultural practices, promote the emission of tons of atmospheric particles (PM). In order to have a better understanding about the toxics contained in the particle emission from sugarcane burning, two sampling campaigns to collect fine particles (PM$_{2.5}$) and respirable particles (PM$_{10}$) during and after the harvest season, were performed in the municipality of Córdoba, Veracruz, México, a small city next to many sugarcane crops. Results showed that particles concentrations increased around 41% for PM$_{10}$ and 32% for PM$_{2.5}$, whereas black carbon concentrations increased 25% and 28% respectively. The high PM$_{2.5}$/PM$_{10}$ ratio of 0.7 during harvest shows that most of the particles and toxic are contained in the fine fraction, in addition, the sum of carcinogenic polycyclic aromatic hydrocarbons (PAHs) was around 50% of total PAHs, with a BAPeq of 996 pg m$^{-3}$ during harvesting; these results represent an important risk for the neighboring population, consequently authorities and decision makers should attend and implement control strategies.

Index Terms—Sugarcane burning, PM$_{2.5}$, black carbon, PAHs.

I. INTRODUCTION

During 2013, 780,000 ha of crops were harvested in México, producing 61 millions of tons of sugarcane yielding 78.7 ton ha$^{-1}$ [1]. The sugarcane growing is carried out in 15 states, where Veracruz contributes to 36% of National production [2]. The harvest season of sugarcane lasts between 5 to six months, and during this time, tons of pollutants are emitted to the atmosphere due to burning of biomass which facilitate the work of farmers reducing weeds and moving away insects and snakes; in addition after harvesting, wastes are burned in order to prepare the land for the next planting [3].

Among the most important emitted pollutants during sugarcane burning, particles are of concern since, on one hand they include toxic compounds such as polycyclic aromatic hydrocarbons (PAHs), which are semi-volatile species formed by the fusion of two or more benzene rings through a pyrolytic process during incomplete combustion of organic materials [4]. PAHs have a significant importance in the mutagenic activity of atmospheric particles and some of them have been classified as carcinogenic, such as benzo[a]pyrene, benzo[a]anthracene, chrysene, dibenzo[a, h]anthracene,benzo[b]fluoranthene, benzo[k]fluoranthene, and indene[1,2,3-cd]pyrene [5]. On the other hand, the emitted particles contain black carbon which is a known short-lived climate forcer which contributes to global warming; further black carbon has been associated to 2 million of premature deaths, due to inhalation from domestic cooking [6].

Studies in Brazil reported high correlation between sugarcane burning season and the intensification of admission of children to the hospital because of respiratory illness [7], [8]. Information about the environmental sugarcane burning is scarce and is related mainly to researches in Brazil and Colombia [9]-[11]. In México, only was found one study related to this issue, which concluded that people living next to sugarcane crops have more frequent respiratory illness who those in other sites of the State of Puebla [12].

In this paper, two sampling campaigns were carried out close to the sugarcane to compare the concentrations of PM$_{10}$ and PM$_{2.5}$ during harvest and no-harvest season; in addition the quantification of the levels of black carbon and polycyclic aromatic hydrocarbons contained in particles was performed to determine the occurrence of toxic species.

II. METHODOLOGY

A. Sampling

Sampling site is located in the municipality of Córdoba, Veracruz (18° 53’ N; 96° 56’ W) which is located at 860 m above sea level, in the most important sugarcane zone in Veracruz State which comprises 9 sugar mills and around 200,000 inhabitants.

The weather is warm-humid with an average temperature of 19.9°C, ranging from 6°C to 35°C. Fig. 1 shows the location as well as the wind rose during harvest season.

Collection of fine particles (PM$_{2.5}$) and respirable particles (PM$_{10}$) were performed using 20 x 25 cm Whatman quartz fiber filters, previously calcined at 550 °C to remove organic
matter. Filters were placed in Hi Vol equipment’s (Tish Environment) and 24 h integrated samples were collected during 30 days. The samplings in the harvest and no-harvest seasons were in April and July 2013, respectively. After collection, filters were wrapped with foil and stored at -4 °C. Meteorology data were collected in the site with the meteorological station of the Universidad Veracruzana.

B. Analysis

After gravimetric analysis, PAHs were extracted by immersing a piece of filter in an ultrasonic bath (Bransonics) with dichloromethane, thrice for 10 min periods at 10°C. The extracts were concentrated in a rotary evaporator, filter with syringe filters, brought to 1 mL and stored in amber glass vials at -18°C until chromatographic analysis [13]. A gas chromatograph mass spectrometer (GC model HP 6890) with a quadrupole mass filter and an autosampler (model 5 973) was used with a 30 m HP5-MS capillary column (0.25 mm id, 0.25 µm film thickness) for identification and quantification of PAHs. The oven temperature was operated at 65 °C for 2 min, and increased 8 °C/min to 320 °C, held for 10 min. High-purity nitrogen was used as carrier gas at a flow rate of 1 mL min. Fluoranthene d10 was added as internal standard according to Method TO-13A [13]. A standard PAH mixture was used for quantification of: naphthalene (NAP), methylnaphthalene (MNAP), acenaphthylene (ACY), acenaphthene (ACE), anthracene (ANT), phenanthrene (PHE), benzo[a]pyrene (BAP), benzo[b]fluoranthene (BBF), benzo[k]anthracene (BAA), fluorene (FLU), fluoranthene (FLT), pyrene (PYR), chrysene (CRY), benzo[k]fluoranthene (BKP), 2-methylnaphthalene (MNAP), dibenzo[a,h]anthracene (DBA), indene[1,2,3-cd]pyrene (IND), and benzo[g,h,i]perylene (BGP). Further, toxic equivalent factors (TEFs) were applied to estimate the carcinogenic potency of the PAHs mixture.

A Thermal-Optical Carbon Aerosol Analyzer with reflectance correction (Sunset Lab, ForestGrove, OR USA), was used to determine organic and elemental carbon (OC and EC), which were determined by automated thermal-optical transmittance (TOT), using the National Institute for Occupational Safety and Health method (NIOSH) 5040 described by Birch and Cary [14].

C. Statistical Analysis

Medians of pollutants in the two sizes and seasons were compared to establish significant differences in the concentrations measured using the non-parametric Mann-Whitney test. The statistical analyses were carried out with SPSS 22.0 for Windows 2013.

III. RESULTS AND DISCUSSION

Table I displays the basic statistics of particle concentrations, as well as carbonaceous species and total PAHs. Concentrations of PM10 and PM2.5 increased 41% and 32% respectively during harvest concentrations, despite that during harvest season the occurrence of strong winds > 8 m s-1 was frequent favoring the pollutant dispersion. The Mann-Whitney test presented significant differences between PM10 and PM2.5 concentrations during the two periods (p < 0.01), showing statistical increase in the concentration levels of both size of particles. Only two days the 24 h PM10 and PM2.5 Mexican standards (120 μg m-3 and 65 μg m-3, respectively) were exceeded during harvesting time; in opposite, through no-harvest the concentrations of both sizes of particles were never exceeded. The PM2.5/PM10 ratio shows that during harvest 70% of the particles are in the fine fraction which is of concern since these particles can penetrate deeper in the respiratory system. These results are similar to those reported in Araraquara, in Brazil where during harvest the concentration levels ranged from 41 to 182 μg m-3, while during no-harvest concentrations were 12 to 41 μg m-3 [9].

The quantification of black carbon (BC) has gained attention in the last years since the World Health Organization reported that cohort studies have provided enough evidence of associations of all-cause and cardiopulmonary mortality with long-term average BC exposure [15]. The terms black carbon and elemental carbon are often used interchangeable, but there is a difference related to the analytical method used. Black carbon refers to the dark, light-absorbing components of aerosols, whereas elemental carbon is measured with an analytic thermal method [16], nevertheless, in the reports of the Intergovernmental Panel of Climate Change (IPCC) only the term black carbon is used regardless the measurement method [17]. It has been stated that black carbon is the second cause of global warming since the radiative forcing of BC in a period of 20 years is 2200 times higher than the global warming power of CO2 [18].

### Table I: Descriptive Statistic of Measured Pollutant Concentrations

| Pollutant | Harvest | No Harvest |
|-----------|---------|------------|
| PM10 μg m⁻³ | MEAN | MAX | MIN | MEAN | MAX | MIN |
| OC10 μg m⁻³ | 16±8.1 | 33.6 | 7.7 | 7.7±2.2 | 11.6 | 2.2 |
| BC10 μg m⁻³ | 4.9±1.0 | 6.7 | 1 | 3.7±1.0 | 6.3 | 2.7 |
| TC10 μg m⁻³ | 19.8±9.7 | 40.2 | 8.5 | 10.9±1.1 | 16.5 | 3.1 |
| ∑PAH10 in ng m⁻³ | 6.17±0.99 | 9.23 | 4.38 | 3.46±0.86 | 4.89 | 2.13 |
| PM2.5 μg m⁻³ | MEAN | MAX | MIN | MEAN | MAX | MIN |
| OC2.5 μg m⁻³ | 13.8±2.9 | 18.1 | 3.8 | 5.1±1.6 | 6.3 | 4.2 |
| BC2.5 μg m⁻³ | 3.2±0.6 | 6.3 | 1 | 2.3±0.4 | 2.9 | 1.6 |
| TC2.5 μg m⁻³ | 16.2±3.9 | 22.5 | 10.4 | 7.3±1.1 | 9.3 | 5.8 |
| ∑PAH2.5 in ng m⁻³ | 5.03±0.71 | 6.97 | 3.86 | 2.72±0.61 | 4.11 | 1.94 |
| PM2.5/PM10 | 0.74±0.1 | 0.86 | 0.34 | 0.6±0.1 | 0.81 | 0.4 |
| OC2.5/OC10 | 0.9±0.1 | 0.93 | 0.09 | 0.7±0.1 | 0.75 | 0.6 |
| BC2.5/BC10 | 0.7±0.1 | 0.81 | 0.08 | 0.6±0.1 | 0.76 | 0.6 |
| TC2.5/TC10 | 0.9±0.1 | 0.93 | 0.07 | 0.7±0.1 | 0.76 | 0.6 |
| ∑PAH2.5/∑PAH10 | 0.82 | 0.90 | 0.75 | 0.79 | 0.84 | 0.76 |

Total carbon was 1.8 and 1.5 times higher during the harvest period for PM10 and PM2.5 respectively; organic carbon concentration levels were 2.1 times greater for PM10.
and 2.7 times for PM$_{2.5}$ during harvest, whereas black carbon increased 1.3 and 1.4 times respectively contributing with the 5% of the total mass of PM$_{10}$ and 7% of the total mass of PM$_{2.5}$.

The BC level concentrations measured in this study are in agreement with the reported concentrations in Southeastern Brazil [19]. Concentrations of total carbon, organic carbon and black carbon during harvest and no harvest were statistically different for both sizes of particles.

The measured increases observed in black carbon suggest that sugarcane burning is not only a health concern but also a climate worry for the positive radiative forcing that increases global warming. Regarding the total PAH concentrations, the levels were 1.8 and 1.9 times greater for PM$_{10}$ and PM$_{2.5}$ respectively, during harvest than no harvest period, exhibiting statistical differences ($p < 0.05$).

The high ratio of PM$_{2.5}$/PM$_{10}$ (0.7) means that 70% of particles are in the fine fraction, whereas 90% and 82% of OC and PAHs are in that fraction that can penetrate deeper in the lungs. Despite the PM$_{10}$ concentrations measured in this study are quite similar to those measured in Araraquara, Brazil, the total PAHs concentrations in Veracruz were lower than the 11.6 ng m$^{-3}$ reported in Brazil during harvest and 3.5 ng m$^{-3}$ during no-harvest [9]; other study in the same city in Brazil [20] reported also high average concentrations of total PAHs with 25.9 ng m$^{-3}$ during harvest. The most abundant PAHs were IND, BBF, BAP, BGP, PYR and FLT, whereas ANT, FLU and ACE showed the lowest concentrations (Fig. 2).

During harvest, the sum of carcinogenic PAHs (BAP, BAA, BBF, BFK, CRY, DBA and IND) was 3.1 ng m$^{-3}$ for PM$_{10}$ and 2.59 ng m$^{-3}$ for PM$_{2.5}$, which is equivalent to 50% of total PAHs. These values are 1.8 and 1.9 higher than the sum of carcinogenic PAHs during no-harvest, 1.7 ng m$^{-3}$ and 1.3 ng m$^{-3}$ for PM$_{10}$ and PM$_{2.5}$ respectively. These results suggest that the risk of cancer increases during harvesting, since half of PAHs concentrations are associated to the seven carcinogenic PAHs. In addition, the emitted PAHs could have secondary reactions in the atmosphere and produce nitro PAHs, chlorinated PAHs and o xo PAHs, which in general have a greater mutagenic activity in comparison with their precursors, maybe due to a greater polarity [21].

For more than 25 years BAP has been considered the reference PAH for whole PAH carcinogenicity. The European Union proposed 1 ng m$^{-3}$ as an annual average for BAP in PM$_{10}$ [22], whereas 0.25 ng m$^{-3}$ is the annual average air quality standard in the United Kingdom [23]. The mean obtained for BAP during harvest was 0.49 ng m$^{-3}$ which exceeds the United Kingdom standard but not that of European Union, in opposite, in no-harvest the mean concentration of BAP was 0.24 ng m$^{-3}$. Table II shows the comparison of BAP concentrations measured in this study with those reported in other studies developed in rural areas where sugarcane is grown, as well as with the levels found in some cities. In general, BAP concentrations in PM$_{10}$ of this study are in agreement with similar researches in sugarcane zones, and the concentrations of this PAH is higher than in big cities such as Porto Allegre, Hong Kong and Mexico City.

Some of the other PAH could have a medium or high carcinogenic potency, which suggested that the merely determination of BAP could be insufficient; hence, toxic equivalent factors (TEF) were developed with the aim of estimating the carcinogenic potential of different PAHs in terms of BAPeq carcinogenicity, multiplying the concentrations of each PAH by the corresponding TEF [22].

Table II presents the TEFs for each average value of PAHs developed by Nisbet and La Goy [24], as well as the estimation of BAPeq in the mixture. It is possible observe that the maximum value was obtained during harvest PM$_{10}$ although the BAPeq is equal to the standard proposed by the European Union of 1 ng m$^{-3}$, it is relevant to mention that the population is exposed for six months straight, and the

![Fig. 2. Concentrations of individual PAH in two sizes of particles and both seasons.](image)
mentioned standard was designed for an annual exposure with variations in the PAH concentrations among the days.

IV. CONCLUSIONS

The exposure to PM$_{10}$ and PM$_{2.5}$ of the neighboring population to sugarcane crops was respectively 1.7 and 1.5 times higher during the harvest period than in the no harvest, increasing the health risk. These particles contain toxic species such as black carbon and polycyclic aromatic hydrocarbons.

According with the PM$_{2.5}$/PM$_{10}$ ratios, 70% of particles and BC are in the PM$_{2.5}$ fraction, whereas in the case of PAHs 82% are in the fine fraction, which increases the risk to respiratory illness, due that fine particles can penetrate deeper in the lungs.

The increase of black carbon and carcinogenic organic compounds, such as PAHs must be considered in the risk assessment conducted by health authorities, not only PM$_{10}$ and PM$_{2.5}$.

Level concentrations of black carbon during harvest were 25% and 28% greater for PM$_{10}$ and PM$_{2.5}$, which in addition to the health risk for population, have implications in global warming; therefore, integrated policies which address climate change and air pollution health effects are required for an effective control of these emissions.

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