Atmospheric Environment 193 (2018) 262–272

Contents lists available at ScienceDirect

Atmospheric Environment

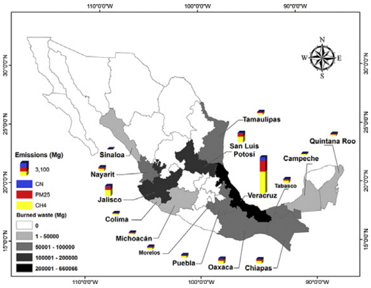
journal homepage: www.elsevier.com/locate/atmosenv

Sugarcane burning emissions: Characterization and emission factors

Violeta Mugica-Álvarez[a,*], Francisco Hernández-Rosas[b], Miguel Magaña-Reyes[c], Jorge Herrera-Murillo[d], Naxieli Santiago-De La Rosa[a], Mirella Gutiérrez-Arzaluz[a], José de Jesús Figueroa-Lara[a], Griselda González-Cardoso[a]

[a] Universidad Autónoma Metropolitana-Azcapotzalco, San Pablo 180 Ave., Col. Reynosa-Tamaulipas, 02200, CDMX, Mexico
[b] Colegio de Postgraduados, Campus Córdoba, Veracruz, Mexico
[c] Instituto Nacional de Ecología y Cambio Climático, CDMX, Mexico
[d] Universidad Nacional de Costa Rica, Costa Rica

GRAPHICAL ABSTRACT



ARTICLE INFO

Keywords:
Emission factors
Sugarcane burning
$PM_{2.5}$
VOC
PAH

ABSTRACT

Open burning of sugarcane (*Saccharum officinarum*) has a large impact in regional atmospheric pollution and global climatic change. In this research, pollutant emissions from sugarcane residues burning were measured in order to determine the emission factors (EFs) of elemental carbon (EC), organic carbon (OC), 18 polycyclic aromatic hydrocarbons (PAHs), K, Na, Ca, Mg, NO_3^-, SO_4^{2-}, NH_4^+, and Cl^- contained in particulate matter (PM), as well as EFs of the gaseous pollutants, carbon dioxide (CO_2), carbon monoxide (CO), methane (CH_4) and 37 volatile organic compounds (VOCs). Experiments were carried out in an open combustion chamber equipped with isokinetic sampling, following EPA 5 and modified EPA 201-A methods. Preliminary tests showed that continuous feeding of residues does not represent the open burning carried out in the field since flaming stage is sustained, thus batch feeding of residues was used to perform around 30 experiments. Gaseous pollutants EFs were 1618 ± 108, 25.7 ± 2.04 and 2.29 ± 0.13 g kg^{-1} for CO_2, CO and CH_4 respectively, while C_2 compounds have the highest EF of VOCs. PM_{10} and $PM_{2.5}$ accounted for 55% and 36% of total PM mass, whereas carbonaceous species (EC and OC) accounted for 66% in $PM_{2.5}$ and 58% in PM_{10} and total PM mass. Emission factors of EC varied from 0.34 to 0.37 g kg^{-1}, and EF of OC were 0.44, 0.67 and 1.2 g kg^{-1} for $PM_{2.5}$, PM_{10} and total PM, respectively. Highest EFs of determined elements and anions were K and Cl^-, respectively. Heavy PAHs such as benzo[*b*]fluoranthene, bezo[*k*]fluranthene and benzo[*a*]pyrene presented the greatest EFs with 0.265 ± 0.04, 0.264 ± 0.08 and 0.254 ± 0.015 mg kg^{-1} respectively. Kruskal Wallis tests indicated that EFs had no significant differences among sugarcane varieties harvested in sites with different altitudes and climate, thus they can be applied for inventories estimations in world regions similar to Mexico, as well as in air quality forecasting models and climatic model allowing a better knowledge of air pollution and climatic change

---

[*] Corresponding author.
E-mail addresses: vma@correo.azc.uam.mx, vma@azc.uam.mx (V. Mugica-Álvarez).

https://doi.org/10.1016/j.atmosenv.2018.09.013
Received 6 March 2018; Received in revised form 9 August 2018; Accepted 10 September 2018

scenarios. The results of this research can be the base to design and establish public policies in order to regulate and eventually eliminate the practices of pre-harvest and post-harvest sugarcane burning.

1. Introduction

Agriculture fire is a common practice used by farmers, to control crop diseases and plagues, as well as to prepare the land for the next crop (Hays et al., 2005; Sanchis et al., 2014). Sugarcane is the only crop which fire is used pre-harvesting in both, developed and developing countries, to expose the cane stalks removing the outer leaves, driving away insects, snakes and other wild animals making easy not only manual, but also mechanical harvesting (Sevimoglu and Rogge, 2015); additionally, after harvesting, sugarcane residues are burned releasing to the atmosphere more harmful pollutants (Neto et al., 2011). Mexico is the 6th sugarcane producer in the world where more than 92% of harvesting is performed with the use of fire from November to May, because this industry is highly protected, since it represents an important economic income for the country and provides direct employment to around 500,000 people and more than 2 million indirect jobs (Conadesuca, 2017). Biomass burning has several negative environmental impacts: a) the emission of greenhouse species like CO_2, CH_4 and black carbon which contribute to global climate change and variations in the hydrology cycling and regional climate (Kaufman et al., 2002; Ramanathan and Carmichael, 2008); b) the emission of harmful air pollutants that degrade regional air quality (Crutzen and Andreae, 1990; Koppmann et al., 2005; Fitzpatrick et al., 2007) and damage the health of the nearby population and the harvesters (Cançado et al., 2006; Tsiouri et al., 2015) c) soil degradation due to elimination of beneficial microflora and the loss of organic matter and micronutrients, especially N and S (Stirling et al., 2010; Singh and Sidhu, 2014).

Among the climatic pollutants emitted to the atmosphere during sugarcane burning, the black carbon (BC) and methane considered short-lived climate pollutants (SLCPs) stand out, because they remain in the atmosphere for a much shorter period than longer-lived climate pollutants as is CO_2. SLCPs, which include also tropospheric ozone and some hydrofluorocarbons, have gained attention since estimations show that they may be responsible for 40–45% of overall global warming (Bond et al., 2013). BC is a major component of soot, it is produced during incomplete combustion of organic matter, and it is the second leading cause of global warming since is a climate-forcing aerosol that remains in the atmosphere for only a few days or weeks (Badarinath et al., 2009; Chung et al., 2012; Bond et al., 2013). Recent evidences suggest that the mitigation of SLCPs can reduce the rate of warming in the short term and improve air quality and public health (UNEP-WMO, 2011), since BC is always associated with other substances generated during biomass combustion like organic compounds (OC), PM, CO, nitrogen oxides (NOx), VOCs, and PAH, among others, which produce severe effects to the health (Chen et al., 2017).

Studies related to the emissions generated by sugarcane burning in Latin America have reported that during harvesting, atmospheric concentrations of $PM_{2.5}$, PM_{10} and BC increased from 2 to 4 times while PAH concentrations were up to six times greater with the consequent increase in cancer risk potential (De Andrade et al., 2010; Silva et al., 2010; Prado et al., 2012; Cristale et al., 2012; Cárdenas et al., 2014; Mugica-Álvarez et al., 2015), additionally Mugica-Alvarez et al. (2017) determined the increase of PM_{10} and $PM_{2.5}$ during harvesting and modeled the dispersion of $PM_{2.5}$ and PAHs emitted during sugarcane burning using factor emissions from literature showing that towns downwind have very high instantaneous exposures to those pollutants. Recently, the assessment of mutagenicity of sugarcane burning particles showed that PAH and nitro-PAH contribute significantly to DNA damage (De Oliveira Alves et al., 2014; De Oliveira Galvão et al., 2018). Epidemiological studies have revealed that emissions from sugarcane burning lead to an increase in respiratory and hypertension hospital admissions (Cançado et al., 2006, Uriarte et al., 2009; Arbex et al., 2007, 2010). Regarding studies performed with sugarcane workers, Crowe et al. (2013) reported high exposure levels to heat stress which can cause severe dehydration, Santos et al. (2015) found acute renal dysfunction in previously healthy workers, whereas Silveira et al. (2013) found that cane cutters developed a significant degree of genotoxicity due to the inhalation of sugarcane burning emissions.

To design control strategies, policy makers require accurate EFs of atmospheric pollutants to construct better Emission Inventories and develop mitigation programs, but studies related to EFs from sugarcane burning are scarce. The first EFs from sugarcane burning were determined by Darley (1974), which were applied by the Environmental Protection Agency for the National Inventories (USEPA, AP-42, 1992), until were updated in 2014 (NEI-EPA, 2014). Yokelson et al. (2008) determined $PM_{2.5}$ and gases EFs from a single laboratory sugarcane fire, França et al. (2012) determined also $PM_{2.5}$ and gases EFs during sugarcane straw burning under controlled conditions, whereas Hall et al. (2012) determined EFs of gases, $PM_{2.5}$ and species such as EC, OC and PAHs during continuous burning of sugarcane from Florida. More recently Zhang et al. (2013) measured EFs of gases, $PM_{2.5}$, and some species from rice and sugarcane leaves burning aided by a self-designed dilution chamber system, whereas Stockwell et al. (2014), burned a large variety of biomass fuels, including sugarcane to characterize and determine EFs. These studies have resulted in different EFs values for the same species, due to differences in burning chambers or stoves, burning conditions, sampling of fuels and analytical methods. EFs used in Mexico reported by Andreae and Merlet (2001) and recommended by

Table 1
Physicochemical properties of sugarcane residues.

Sugarcane Variety	Mex 69-290	Mex 69-290	CP 72-2086	CP 72-2086
Site (UTM)	Chiapas (n = 4) 15.120775–92.455771	Jalisco (n = 4) 20.640595–103.71535	Veracruz (n = 4) 18.902901–96.778481	Morelos (n = 4) 18.650602–99.200362
Carbon (%)	44.88 ± 0.42	45.19 ± 0.58	45.55 ± 0.28	43.69 ± 0.51
Hydrogen (%)	5.94 ± 0.18	6.03 ± 0.40	5.93 ± 0.05	5.85 ± 0.13
Nitrogen (%)	0.43 ± 0.12	1.19 ± 0.03	0.43 ± 0.05	0.38 ± 0.08
Sulfur (%)	0.16 ± 0.13	0.29 ± 0.10	0.27 ± 0.07	0.25 ± 0.04
Oxygen (%)	48.60 ± 0.70	47.30 ± 0.31	48.34 ± 0.22	49.83 ± 0.26
Moisture %	10.59 ± 0.39	9.50 ± 0.36	11.21 ± 0.68	10.40 ± 0.47
Cellulose (%)	44.08 ± 0.90			
Hemicellulose (%)	34.16 ± 0.84			
Lignine (%)	11.15 ± 1.25			
HHV (Mj kg^{-1})	20.80 ± 1.39			

HHV: Higher heating value. Uncertainties are reported as standard deviation.

the International Panel of Climatic Change (IPCC) could not represent realistic emissions from sugarcane burning, thus causing uncertainties in the emission inventories, as well as in the application of air quality models in zones impacted by those emissions. Therefore, the main objective of this study was the quantification of EFs for particulate matter (total suspended particle (TSP), PM_{10}, $PM_{2.5}$, EC, OC and PAH), gaseous atmospheric pollutants (CO_2, CO, CH_4 and VOC) simulating open field sugarcane burning of two different varieties collected in various states of the country, using an isokinetic standardized method for sampling with further analysis, to estimate more accurate climatic and atmospheric emission inventories, and improved air quality modeling results. Finally, EFs were employed to determine the emissions of gaseous and PM due to sugarcane burning in Mexico.

2. Methodology

Sugarcane residues from two different varieties were collected in four different geographic regions of Mexico from February to April 2016 in different plots (Table 1). Samples were stored in plastic bags and cut in 10–15 cm pieces, then they were dried outside until reaching a moisture content between 7% and 13% before performing any essay, since that is the range of moisture of more than 50 sugarcane residue samples found in the field (UNE-EN 14774-1, 2010). Cellulose (Kurschner and Hoffer, 1993), hemicellulose (ASTM D1104-56, 1978) and lignin (T222 OM-02, 2006) were determined in triplicate in free organic extracts (TAPPI T204 cm-97, 2007). Elemental composition (C, H, O, S) was measured also in triplicate with a Perkin Elmer PE 2400 analyzer and the higher heating value (HHV) was determined in a PARR 1108 pump calorimeter according to Designation D2015-00 (ASTM, 2000).

Essays were performed in an open combustion chamber for simulation of sugarcane burning in agricultural fields, without extra oxygen feed (Fig. 1), described previously in Santiago-De la Rosa et al. (2018); over the combustion chamber a hood was located connecting a chimney duct, to displace vertically the particulate matter ($PM_{2.5}$ and PM_{10}) and combustion gases up to the sampling point. After several trials to find optimal burning conditions and to avoid filter saturation, the waste mass was established between 0.7 and 0.9 kg with a burning duration of 5–6 min. All essays of each sugarcane variety were carried out at least in triplicate.

An isokinetic analyzer (APEX, SB2), was used to collect the particulate matter employing EPA's Method 5 for total suspended particle (TSP) collection and the modified 201-A method of Federal Code of Regulations No. 40, Part 60, of the United States Environmental Protection Agency (U.S. EPA, 2017) using $PM_{2.5}$ and PM_{10} cyclones (Apex Inst) where quartz fibers were installed to collect particles of the respective aerodynamic size (Environmental Supply Company).

The isokinetic EPA Method 201A (as well as the version modified that includes $PM_{2.5}$) works on the basis of particle inertia to separate size fractions from a gas sample that is extracted at constant flow rate. Depending on its size and velocity, a particle can be directed by a specially sized cyclone for collection in the cyclone hopper where particles are collected in a filter for further determination of gravimetric mass collected (U.S. EPA, 2017). Due to the change in sampling rate affects particle velocity, methods employing cyclones are not carried out at true isokinetic conditions, but rather at fixed sampling rate in which the nozzle velocity is at near average stack velocity during the complete sample duration. Thus the isokinetic acceptance for EPA 201-A is set at ± 20% (Goodarzi, 2006; U.S. EPA, 2017). In order to determine the velocity of the stack gas (v_s) and the total volume of gases, among other parameters, measurements of volume, temperature, meter box orifice pressure drop, were taken in eight points of the chimney. The operation conditions, measurement procedure and equations for data analysis and evaluation are given in the Federal Register 40 CFR Part 51 (Fed Reg, 2010).

The sampling time was five to six minutes and due to the small diameter of the chimney the two cyclones were not connected in series, since the 201-A method specifies that the two cyclones can be operated separately. U.S. EPA, 2017 Methods 1 to 4 were used to ensure acceptable laminar flow conditions, and to determine temperature (ambient and chimney), air velocity in the stack, volumetric flow rate, moisture content of the stack gas, and the gases molecular weight (Murillo et al., 2017). The analysis of combustion gases (CO, CO_2) was carried out simultaneously using a gas analyzer (Bacharach, 24-7343 Fyrite Insight Plus), calibrated and certified in Bacharach installations one week before the first test, including the certification of standard gases by Praxair Mexico, following EPA Method CTM-34. All thermocouples, manometers and chronometers were properly calibrated and certified by an external metrological laboratory (Evaluaciones Ambientales del Centro S.A de C.V) as a quality control mechanism, more details can be found in (Murillo et al., 2017).

Emitted gases from combustion were collected in Tedlar bags (SKC, 5L) for methane quantification. A methane aliquot (0.6 mL) was injected into a gas chromatograph (Agilent, 6890) with a thermal conductivity detector (250 °C), HP-Plot, Q Capilar column (30 m × 320 μm x 20 μm) in the split mode and determined with a standard curve using a standard gas certified by Praxair. Initial temperature was 60 °C (hold: 2 min) and final temperature 180 °C (15 °C min^{-1}).

Two different experiments were performed to select the best way to simulate the open field burning: in the first, a continuous feeding of

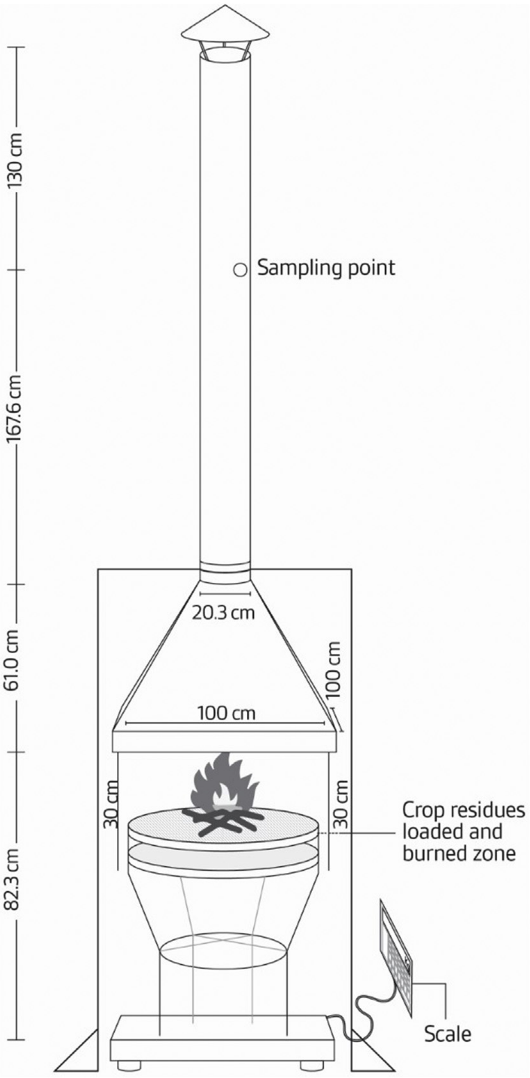


Fig. 1. Schematic diagram of burning device.

residues was provided to maintain the flame and constant burning conditions at a rate of around 130 g every 30 s; whereas in the second, batches of residues (0.6–0.9 Kg) were located in the burner of the combustion chamber; in both experiments temperature was recorded every 45 s in the burner and in the chimney. Pre-baked quartz filters of 825 mm for PST and of 47 mm for PM_{10} and $PM_{2.5}$ were used for particulate matter collection and after sampling they were stored in Petri dishes covered with aluminum foil at −20 °C. Filters were weighed three times before and after sampling with a Mettler Toledo MT5 microbalance (precision of 0.1 mg). Total mass of PST, PM_{10} and $PM_{2.5}$ due to sugarcane burning were obtained dividing the collected mass of particles into the dry gas volume sampled at standard conditions (Vms) and then multiplying by the total volume of gases.

VOC samples were collected in Summa canisters VOC samples were collected in Summa canisters and were analyzed in duplicate with a gas chromatographic system (HP 6890 Series Plus) equipped with a flame ionization detector (GC-FID) that includes a canister rack with a sample controller, humidity controller, and sample concentrator following the USEPA protocols established within the TO-13A method (U.S. EPA, 1999a). Calibration was performed with a certified standard VOCs gas mixture at ambient concentrations (Linde Spectra Environmental Gases), containing 57 ozone precursor VOCs that are diluted up to 0.05–50 ppb in ultra-high purity nitrogen (99.995%) by using a dynamic gas diluter, according to the USEPA protocols including in the TO-14A method (U.S. EPA, 1999b). Measurement detection limits of this system varied from 0.12 for nhexane to 0.39 ppb for isopentane. Calibration curves for the measurement system showed high coefficients of determination ($R2 > 0.99$), indicating high linearity and precision, as well as slopes close to 1, indicating high accuracy (Garzón et al., 2015).

The term black carbon (BC) refers to the dark light-absorbing components of carbonaceus aerosols measured with optical methods, but the term elemental carbon (EC), should be used instead when the carbon content of carbonaceous matter is quantified with a thermal optic method (Petzold et al., 2013). OC and EC concentrations were quantified using an OC/EC Analyzer (Sunset Lab) with NIOSH 870 method (Birch and Cary, 1996). Ionic species (SO_4^{-2}, NO_3^-, NH_4^+ and Cl^-) were analyzed using a Dionex ICS-2500 ion chromatography and elemental composition was determined with Inductively Coupled Plasma with a Thermo iCAP Series 7000 previous to acid digestion with nitric and perchloric acid. Organic matter extraction from ¼ of each filter was carried out twice in an ultrasonic bath at 60 °C (Branson 2510) with 30 mL methylene chloride (grade HPLC, Burdinck & Jackson) during 30 min (Valle-Hernández et al., 2010) in order to determine PAHs in the particulate matter. The extracts were concentrated in rotavapor (BUCHI, 461 Water Bath) to < 30 °C and −5 in Hg followed by evaporation under purified nitrogen to near dryness and reconstituted with acetonitrile. Prior to extraction, a dilution with 6 deuterated PAHs was spiked as surrogate (fluoranthene-d10, phenantrene d-10, pyrene-d10, benzo[*b*]floranthene-d12, benzo[*a*]pyrene-d12 and benzo[*g,h,i*]perylene-d12).

Quantification of PAHs was performed through GC-MS (GC model HP 6890, MS model 5973, Agilent Technologies) see Table 1. PAHs were separated with a capillary column (30 m length x 0.25 mm ID x 0.25 μm film thickness). Twelve PM filters were analyzed and for quality control the urban dust standard reference material (1649a-NIST) was employed to evaluate the recovery efficiency of PAHs which varied from 73% to 111.5%: NAPH (84.2%), 2MNAP (81.4%), ACY (83.1%), ACE (86.6%), FLU (87.8%), PHE (80.3%), ANT (73%), FLT (86.5%), PYR (88.4%), RET (104.6%), BAA (111.5%), CRY (101.4%), BBF (88.2%), BKF (93.6%), BAP (91.8%), PER (103.7%), IND (90.6%), DAA (92.6%), and BGP (92.9%).

Several Quality Assurance and Quality Control (QA/QC) measures were taken to guarantee the integrity of the data. Some of these measures not mentioned above were: field blanks were collected to quantify contamination due to handling and storage procedures; ambient blank samples were collected before each simulated burning to detect background concentrations of analyzed species. Catalytic formation of PAHs can be associated with steel materials as reported by Jenkins et al. (1996), and, although the diameter of the chimney is small, before the experiments conducted to determine PAHs and VOCs the hood and the chimney inner surfaces were covered with aluminum foil to prevent catalytic activity of reactive species.

2.1. Calculation of emission factors

Emission factors of each pollutant (EF_i), was estimated dividing the emitted pollutant mass (m_i) by the dry burnt mass (m_{bm}) (Equation (1)).

$$EF_i = \frac{m_i}{m_{bm}} = \frac{c_i v_t}{m_{bm}} \tag{1}$$

Where;

m_i is the pollutant mass (i = CO, CO_2, CH_4,TSP, PM_{10}, $PM_{2.5}$, VOC, PAH)
c_i is the pollutant concentration
v_t is the total volume of combustion gases

The amount of sugarcane burned on field (M_{sc}) was calculated through the methodology proposed by the IPCC (1996) (Equation (2)). Where, P is the annual production, R is the fraction of the residue-crop product, D is the fraction of dry matter, B is the fraction of residue burned on field and C is the combustion efficiency.

$$M_{sc} = P{*}R{*}D{*}B{*}C \tag{2}$$

Modified combustion efficiency (MCE) is defined as the quantity of carbon released as CO_2, without considering the carbon content of hydrocarbons and particulate matter, and assuming that all carbon was released as CO_2 and CO (Equation (3)) (Ward and Radke, 1993). Where, ΔCO_2 and ΔCO are the concentrations of CO_2 and CO measured during the essays minus the background CO_2 and CO concentrations.

$$MCE = \frac{\Delta CO_2}{\Delta CO_2 + \Delta CO} \tag{3}$$

Combined uncertainty of EFs (UC_{EF}) (Equation (4)) was calculated using the relative uncertainty of the concentration of each pollutant (u_c), total volume of combustion gases (u_{vt}) and burnt mass (u_{mbm}), where c is the concentration of $PM,\ EC,\ OC,\ CO,\ CO_2\ or\ CH_4$.

$$UC_{EF} = \sqrt{u_c^2 + u_{v_t}^2 + u_{m_{bm}}^2} \tag{4}$$

The statistical analyses were performed using SPSS Statistics 20 software. Significant differences among results were determined by the non-parametric Kruskal-Wallis test and Mann-Whitney with a 95% confidence level.

3. Results and discussion

3.1. Physicochemical characteristics of sugarcane residues

Elemental compositions of sugarcane residues collected in different states, as well as other physicochemical properties are shown in Table 1. In general, there are no statistical significant differences in the elemental composition among different samples collected ($\alpha > 0.05$; p value = 0.055, 0.733, 0.061, 0.027 and 0.924 for C, H, N, O, and S respectively); carbon content percentage was in average 44.76 ± 0.81 and moisture percentage was in average 10.43 ± 0.61; Yokelson et al. (2008) reported a C content of 48.8% and 8.58% moisture. Is important to highlight that the HHV measured in this study for the sugarcane straw was 20.8 ± 1.39 Mj kg^{-1} that is indeed similar to the HHV of 20 Mj kg^{-1} and 18.61 Mj kg^{-1} obtained by Das et al. (2004) and Tsai et al. (2006), respectively for bagasse, which is the sugarcane stem residue used as biofuel in the mills.

3.2. Selection of fuel feeding

Through combustion, two major burning stages exist: flaming and smoldering, the former is a greater temperature oxidation process with high combustion efficiency, fire is intense and the fuel ignites producing mainly CO_2 and EC particles formed in the flame from pyrolysis gases. This is consistent with temperature and oxidant-dependent soot formation mechanisms. Conversely, the smoldering stage presents low combustion efficiency due to lower temperatures and lack of oxygen supply, producing CO and other unburned species such as VOCs (Andreae and Merlet, 2001; Tissari et al., 2008; Khan et al., 2009; Mc Meeking et al., 2009).

Fig. 2 presents representative examples of the temperature behavior during the sugarcane residues burning in the two different combustion processes: a) continuous feeding of residues into the chamber; and (b) feeding with residue batches. It is possible to observe that the shape of both traces are quite different: when feeding is continuous burning conditions are maintained almost constant in the 500 °C–600 °C (680–880 K) temperature range in the burner, maintaining the flaming stage between 250 °C and 400 °C (500–650 K) in the chimney; but during batch burning the conditions change throughout the experiment, showing the transition from the flaming stage to that of smoldering at the end of the experiment. Burning duration was longer in batch feeding than in continuous feeding. EFs also presented differences in both combustion processes as observed in Table 2 where the results of TSP, OC and EC EFs of each kind of residue feeding are shown. When continuous feeding was performed MCE reached 0.987 ± 0.003 in average obtaining greater EFs for TSP and EC, but lower CO than in batch feeding. Sugarcane biomass as fuel is continuously fed in stoves, nevertheless the behavior of sugarcane open burning is alike to batch feeding, since the flaming stage is not maintained during the burning process. Thus, all the other experiments were conducted using the batch feeding process.

3.3. Emission factors of gaseous pollutants

3.3.1. EFs of greenhouse gases and carbon monoxide

Table 3 displays the EFs average obtained for CO_2, CH_4 and CO, and the MCE average of 26 tests, as well as their comparison with other researches carried out in laboratory experiments related to sugarcane burning. EFs as well as MCE values did not present significant differences among species and residues collected in several sites ($\alpha > 0.05$; p-value = 0.875, 0.226, 0.666, 0.683 for CO, CO_2, CH_4, and MCE, respectively). The high MCE value and CO EF are similar to those obtained by Yokelson et al. (2008), but CO EF of this study ($25.7 \pm 2.04\ g\ kg^{-1}$) is lower than other studies such as that obtained by França et al. (2012) of $65 \pm 14\ g\ kg^{-1}$ since the MCE estimated in the last research was lower (0.928) and the moisture content of sugarcane residues was higher (16.6–49.4%) affecting the production of particulate matter. The CO EF of this study is higher than that reported by Hall et al. (2012) in three burning events, but these authors reported a higher MCE and employed dry biomass that burns faster. Regarding GHG, the obtained values of CO_2 and CH_4 EFs are in the range of EFs reported in the literature.

Table 2
Preliminary tests for comparison of EFs using two different combustion processes.

	EFs with continuous feeding (n = 3)	EFs with batches feeding (n = 3)
TSP	6.95 ± 0.81	3.33 ± 0.46
OC_T	0.43 ± 0.16	1.44 ± 0.90
EC_T	0.95 ± 0.17	0.39 ± 0.05
OC_T/TC_T	0.45 ± 0.07	0.79 ± 0.08
OC_T/EC_T	0.31 ± 0.03	3.69 ± 0.56
CO	26.2 ± 2.8	14.39 ± 4.03
MCE	0.987 ± 0.003	0.965 ± 0.01

n = number of samples. Uncertainties are reported as combined uncertainties.

Table 3
Emission factors ($g\ kg^{-1}$ dry fuel) of gases from sugarcane burning.

	EF This study n = 26	Other authors
Combustion gases		
CO_2	1618 ± 108	1838[a], 1677 ± 111[b], 1255 ± 287[c], 1303 ± 210[d], 1515 ± 177[e], 1153 ± 258[g], 1353 ± 31[h],
CO	25.7 ± 2.04	28.3[a], 57.5 ± 30[b], 9.2 ± 3.3[c], 65 ± 14[d], 92 ± 84[e], 40.1 ± 15.7[f], 73 ± 9[h],
CH_4	2.29 ± 0.13	0.93[a], 3.8 ± 2[b], 2.7[e], 3.15 ± 0.77[h].
MCE	0.96 ± 0.01	0.976[a], 0.985 ± 0.002[c], 0.928[d]

Uncertainties are reported as combined uncertainty.
[a] Yokelson et al., 2008 (sugarcane).
[b] Yokelson et al., 2008 (average biomass).
[c] Hall et al., 2012.
[d] Franca et al., 2012,[d].
[e] Andreae and Merlet, 2001.
[f] USEPA, 1999a,b.
[g] Zhang et al., 2013.
[h] Stockwell et al., 2014.

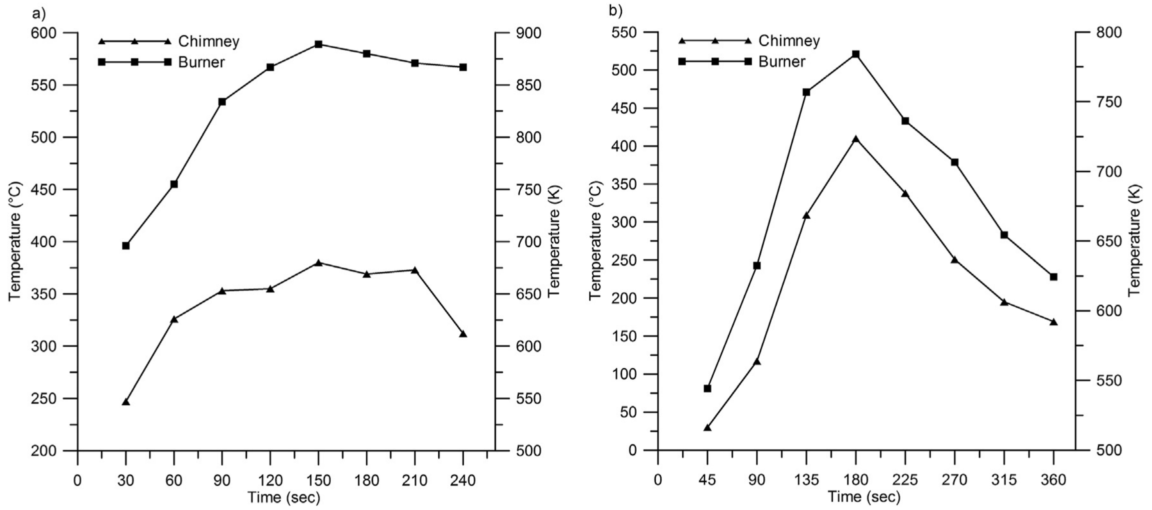


Fig. 2. Temperature evolution during experiments with two biomass feeding procedures. a) continuous (rate: 130 g every 30 s). b) batch feeding (800 g).

3.3.2. Emission factors of volatile organic compounds

As was mentioned above, the knowledge of VOC EFs is fundamental since some of those compounds are toxic and harmful for ecosystems, in addition they are precursors of ozone, considered also a short lived climatic pollutant (SLCP) in conjunction with CH_4, N_2O and BC, which promote substantial regional and global climatic impacts (UNEP-WMO, 2011). Table 4 displays the VOCs profiles of sugarcane burning as emission factors quantified in three combustion scenarios: flaming stage, smoldering stage and complete combustion that include both stages. The sum of VOCs EFs was more than four times greater during the smoldering stage than in the flaming stage, due to incomplete combustion of the former stage, suggesting that in the complete combustion, the smoldering stage at the end of combustion contributed with the greatest VOCs concentrations. The EFs for total VOCs was 7.97 g kg^{-1} for sugarcane residues burning, which is a little higher than those determined for agricultural residues by Andreae and Merlet (2001) and it is more than 25% lower than that reported by Zhang et al. (2013), although some VOCs can be different, presenting different mass. Some VOC EFs are in the order of magnitude than those reported by Yokelson et al. (2008) for sugarcane and average biomass, but BETX (for benzene, ethylbenzene, toluene and xylene) are significantly higher than those reported by Hall et al. (2012), perhaps because in that study the combustion efficiency was greater.

Table 5
Comparison of major species from sugarcane burning (vol %).

VOC	This study n = 2	Zhang et al., 2013 n = 1
ethane	22.13	27.91
ethene	38.86	8.01
ethyne	6.71	5.86
propane	11.25	7.40
propene	3.73	3.45
1-butene	1.60	1.99
n-butane	3.91	4.12
ibutane	2.11	2.44
ipentane	1.61	3.19
n-hexane	1.45	2.43
benzene	4.50	2.19
toluene	2.80	2.55
ethylbencene	2.82	1.18
isoprene	0.89	3.19
m/p xylene	2.07	2.10

The sum of C_2 and C_3 accounted for 71% of the total VOCs volume,

Table 4
Emission factors (g kg^{-1} dry fuel) of VOCs from sugarcane burning. Bold: Flame plus smoldering stages.

	EF in Flame stage n = 2	EF in Smoldering stage n = 2	EFs during complete combustion n = 2	Other authors
ethane	0.22	1.97	**0.95**	
ethene	0.50	11.41	**1.90**	0.63[a], 1.83 ± 1.19[b], 2.13[e]
propane	0.94	1.36	**0.72**	
propene	0.17	2.82	**0.26**	0.561 ± 0.332[b]. 0.71[e]
isobutane	0.10	0.15	**0.19**	
n-butane	0.27	0.43	**0.35**	
ethyne	0.29	4.30	**0.27**	0.072[a], 0.334 ± 0.30[b], 0.84[e]
t-2-butene	0.00	0.13	**0.03**	
1-butene	0.03	0.51	**0.14**	
cyclopentane	0.01	0.26	**0.04**	
c-2-butene	0.00	0.09	**0.03**	
isopentane	0.14	0.30	**0.18**	
n-pentane	0.04	0.24	**0.15**	
t-2pentene	0.03	0.00	**0.06**	
1-pentene	0.03	0.05	**0.01**	
methylciclpentane	0.04	0.07	**0.01**	
cyclohexane	0.13	0.69	**0.15**	
c-2-pentene	0.16	0.06	**0.11**	
2,2-dimethylbutane	0.15	0.09	**0.09**	
3-methylpentane	0.05	0.00	**0.00**	
n-hexane	0.13	0.30	**0.05**	
isoprene	0.15	0.04	**0.19**	
1-hexene	0.07	0.19	**0.06**	
methylciclohexane	0.21	0.07	**0.06**	
2,4-dimethylpentane	0.11	0.03	**0.04**	
2,3 dimethylpentane	0.32	0.06	**0.10**	
n-heptane	0.08	0.04	**0.12**	
isooctane	0.27	0.00	**0.19**	
234-trimethylpentane	0.26	0.15	**0.08**	
3-methylpentane	0.16	0.08	**0.01**	
2-methylheptane	0.10	0.00	**0.00**	
n-octane	0.15	0.07	**0.07**	
n-nonane	0.10	0.06	**0.06**	
benzene	0.54	1.78	**0.29**	0.207[a], 0.65[b], 0.017[c]
toluene	0.39	1.44	**0.30**	0.12[a], 0.56[b], 0.005[c]
ethylbenzene	0.49	1.34	**0.46**	0.06[a], 0.18 ± 0.11[b], 0.00081[c]
xylenes (m + o + p)	0.23 (m + p)	0.001 (m + p)	**0.25**	0.115[a], 0.34 ± 0.19[b], 0.0012[c]
Σ VOCmeasured	7.07	30.58	**7.97**	16 ± 6[d],11.02[g], 7[f]

o: orto-xylene, m: metaxylene, p: paraxylene
[a] Yokelson et al., 2008 (sugarcane).
[b] Yokelson et al., 2008 (average biomass).
[c] Hall et al., 2012.
[d] Franca et al., 2012 (includes CH_4).
[e] Stockwell et al., 2014.
[f] Andreae and Merlet., 2001 (agricultural residues).
[g] Zhang et al., 2013.

whereas the BTEX contributed with 11.7 ± 0.1%. Ethene, ethyne and propene EFs quantified by Stockwell et al. (2014) are 1.1, 3.1 and 2.7 larger than those obtained in this study, but values of emission ratio of each VOC to CO (mol/mol) are quite similar: 0.12, 0.012 and 0.011 (reported by Stockwell et al., 2014) vs. 0.08, 0.011 and 0.011 (calculated in this study) for ethene, ethyne and propene, respectively, showing that standardization with CO allows a better comparison among the studies.

Although the comparison is difficult with other studies, since different analytical techniques are used and the individual VOCs measured could not be the same, the major VOCs species quantified in this study are alike those presented by Zhang et al. (2013), as shown in Table 5 that presents the comparison of the 15 most abundant VOCs measured in this work. It is possible to observe similarities between the two studies, although in this research the contributions of ethane, ethyne, propane and aromatic species were higher. The toluene/benzene ratio of 0.72 is closer to the value reported by Hedberg et al. (2002) of 0.5 for wood combustion than the value of around 3 reported by Kristensson et al. (2004) for vehicle exhaust.

3.4. Emission factors of particulate matter

3.4.1. Emission factors of TSP, PM_{10}, $PM_{2.5}$, EC and OC

The percent isokinetic sampling for PST had an average of 93.1% with a range between 85.3% and 105.8%; in the case of PM_{10} had an average of 96.3% with a range from 88.4% to 117.9%, while the $PM_{2.5}$ isokinetic sampling reported a higher percent with an average of 112.7% with a range from 102% to 118.5%; it has been reported that overisokinetic sampling is preferred to subisokinetic sampling, and ISO standard 23210 (2009), that use impactors to enable simultaneous measurement of PM_{10} and $PM_{2.5}$, considers that the selected nozzle must achieve an isokinetic sampling rate between 90 and 130% of the exact isokinetic velocity (Lamminen, 2010).

Emission factors of TSP, PM_{10} and $PM_{2.5}$, and those of OC and EC are shown in Table 6. $PM_{2.5}$ accounted for 66% of PM_{10} fraction, whereas the latter contributes with 55% of total particulate matter. Organic carbon was 76%, 61% and 56% of total carbon species in TSP, PM_{10} and $PM_{2.5}$ respectively. With the exception of TSP, PM EFs are in general lower than those reported by other researchers, probably due to differences in combustion protocols and/or moisture content since it has been reported that this parameter affects the production of particulate matter (Sanchis et al., 2014). Yokelson et al. (2008), conducted one test for sugarcane using a combustion chamber of 12.5 m × 12.5 m × 22 m whereas Hall et al. (2012), used a combustion chamber quite similar to that employed in this study, although in those cases the fire burned in a continuously-weighted fuel bed, which could emit more EC as was shown above. Note that França et al. (2012), reported a lower combustion efficiency, namely 0.928, but since the moisture content of their residues was greater than those presented here, between 16.6% and 49.4%, a larger emission of incomplete combustion products was promoted, additionally they forced trace gases exhaustion applying an outer stack fan. EC/OC EFs ratios were 3.24, 1.81 and 1.27, for TSP, PM_{10} and $PM_{2.5}$, respectively, according with most of the biomass burning researches where OC used to dominate carbonaceous aerosols (Akagi et al., 2011, Mc Meeking et al., 2009), conversely Hall et al. (2012), reported a very unique high EC relative to OC ratio for dry sugarcane burning of 0.28. Nonetheless, our experiments conducted with biomass continuous feeding are alike the EFs obtained by Hall et al. (2012), for carbonaceous aerosol with an EFs OC/EC ratio of 0.45 (Table 2), who also performed the experiment with biomass continuous feeding. It is important to remind that the combustion process with continuous fuel feeding could not represent adequately the open burning, since the flaming stage is maintained longer. In general neither PM EFs nor EC and OC EFs exhibited significant differences for different varieties of sugarcane ($\alpha > 0.05$) as is shown in Table 6, suggesting that these can be useful not only in Mexico, but also in sites with similar weather conditions to those presented in Table 1. The emission factors obtained in this study under controlled and confined conditions at pilot level can represent an average of sugarcane burning emissions in the field when the weather is dry and meteorological conditions show low wind speed (that is a requirement for farmers to be allowed to burn to avoid firings).

3.4.2. Emission factors of elements and ions

Table 7 displays the EFs for Na, K, Ca and Mg, as well as EFs of water-soluble ions in $PM_{2.5}$. The sum of both, elements and ions measured, accounted for 45.5% of $PM_{2.5}$ mass, and these emissions are enriched in Cl^- and K; these results are similar to sugarcane emission outcomes of Zhang et al. (2013). It has been reported that straw could be burnt together with bagasse in boilers since carbon and nitrogen content as well as HHV are alike, but the higher chlorine content in the straw could cause corrosion to the boilers and the high potassium content could produce deposits as well as surface corrosion (Leal et al., 2013).

Table 6

Emission factors (g kg^{-1} dry fuel) of particulate matter from simulated sugarcane burning.

	This study	p-value ($\alpha > 0.05$) Kruskal Wallis test	Other studies
TSP	3.27 ± 0.81 (n = 30)	0.543	2.3–3.5[c]
OC_T	1.2 ± 0.09 (n = 30)	0.112	
EC_T	0.37 ± 0.10 (n = 30)	0.098	
OC/TC_T	0.76 ± 0.10		
PM_{10}	1.81 ± 0.14 (n = 12)	0.054	5.65 ± 1.30[f]
OC_{10}	0.67 ± 0.36 (n = 12)	0.130	
EC_{10}	0.37 ± 0.10 (n = 12)	0.996	
OC/TC_{10}	0.61 ± 0.13		
$PM_{2.5}$	1.19 ± 0.08 (n = 12)	0.192	2.17[a]; 2.5 ± 0.66[b], 2.6 ± 1.6[d], 3.9[e], 4.12 ± 1.1[f]
$OC_{2.5}$	0.44 ± 0.13 (n = 12)	0.826	0.16 ± 0.09[b], 1.25 ± 0.67[f]
$EC_{2.5}$	0.34 ± 0.09 (n = 12)	0.695	0.71 ± 0.22[b], 1.22 ± 0.66[f]
$OC/TC_{2.5}$	0.56 ± 0.07		

n = number of samples. Uncertainties are reported as combined uncertainty.

[a] Yokelson et al., 2008.

[b] Hall et al., 2012.

[c] U.S. EPA, 1992.

[d] Franca et al., 2012.

[e] Andreae and Merlet, 2001 (all crops).

[f] Zhang et al., 2013.

Table 7
Emission factors of elements and soluble ions in PM$_{2.5}$ (g kg^{-1} dry fuel) from sugarcane burning.

Elements	EFs g kg^{-1}	Comparison EF other studies PM$_{2.5}$
Na (sodium)	0.002 ± 0.001	
K (potassium)	0.213 ± 0.084	1.38[a]
Ca (calcium)	0.000 ± 0.000	0.0 ± 0.0[b]
Mg (magnesium)	0.002 ± 0.001	0.0 ± 0.0[b]
Water soluble ions		
NO_3^- (nitrates)	0.002 ± 0.000	0.0 ± 0.0[b]
SO_4^{-2} (sulfates)	0.040 ± 0.006	0.1 ± 0.1[b]
NH_4^+ (ammonia)	0.026 ± 0.005	0.1 ± 0.0[b]
Cl^- (chloride)	0.256 ± 0.047	0.87[a], 0.4[b]
K^+		0.3 ± 0.1[b]

Uncertainties are reported as combined uncertainty.

[a] Yokelson et al., 2008.

[b] Zhang et al., 2013 (flaming conditions).

3.4.3. Emission factors of polycyclic aromatic hydrocarbons

Table 8 shows the concentrations and EF of PAHs contained in the PM determined with EPA's Method 5. Total PAH concentrations for sugarcane burning was 42.45 ± 3.56 mg m^{-3}, whereas total PAHs EF was 1.678 ± 0.238 mg kg^{-1}. The greater EFs are related with higher molecular weight compounds from 4 to 6 rings. The 4-rings PAHs: FLT, CRY, PYR and BAA accounted for 4.8% of total PAHs EFs; the 5-rings PAHs: BBF, BKF, BAP, PER and DAA accounted for 49.8% of total PAHs EFs and 6-rings PAHs: IND and BGP accounted for 19.8% of total PAHs EFs, whereas EFs of 2 and 3-rings PAHs accounted by 25.7% of total PAHs EFs. These results are the opposite to those of Hall et al. (2012), who reported that low molecular weight compounds (2 and 3 rings) accounted for the total mass of PAHs and that high molecular PAHs were no detected. This can be due to the different sampling techniques since Hall et al. (2012), used a sorbent cartridge containing polyurethane foam (PUF) and XAD-2 resin that can retain and adsorb the gaseous compounds during collection and short time permanence storage (Mugica et al., 2010), whereas in this study only the PAHs in particles were sampled in a quartz filter, then gaseous compounds pass through the PM sampler located close to the chimney at high temperature. The ratio of indeno[*123-c,d*]pyrene/(indeno[*123-cd*]pyrene + benzo[*g,h,i*]perylene) was 0.56, that is similar to the signature found by Ravindra et al. (2008) of 0.62 for wood burning, and quite different for the ratios of diesel (0.37) and light duty vehicles (0.17).

The high EFs of heavier PAHs is consistent with the results found by several researchers during harvesting in Brazil, Colombia and Mexico who found that greater PAH concentrations corresponded to heavier PAHs (Godoi et al., 2004; Silva et al., 2010; Cárdenas et al., 2014; Mugica-Álvarez et al., 2015, Mugica-Álvarez, 2016). Of especial concern is that carcinogenic concentration of PAHs in atmospheric particles such as (benzo[*a*]anthracene, benzo[*b*]fluoranthene, benzo([*k*]fluoranthene, and benzo[*a*]pyrene) was up to 5 times higher in harvesting than in non-harvesting season (Silva et al., 2010; Mugica-Álvarez et al., 2015).

3.4.4. Emission estimates

In the last decade, sugarcane production has remained relatively constant between 42,500,000 and 53,600,000 of Mg: with the exception of 2013 when the reported production was 61,439,000 Mg (Conadesuca, 2017), but due to the potential increase in ethanol production, cropping of sugarcane could be increased because since 2008 a biofuels promotion and development law passed, that established ethanol as an oxygenation additive to gasoline (García et al., 2011).

Table 9 shows the estimation of sugarcane burned in 2016–2017 harvest in Mexico, as well as the PM$_{2.5}$, PM$_{10}$, EC in PM$_{2.5}$, CO, CO$_2$ and CH$_4$ emissions employing the EFs obtained and other previously determined data, based on field inspections and surveys, such as fraction of residue of the crop product, dry matter fraction, residue burned fraction, and combustion efficiency (Mugica-Alvarez et al., 2017). As expected, CO$_2$ exhibited the greatest emissions volume, although these emissions are not taken into account due to CO$_2$ absorption during crop growth in the next agricultural cycle, thereby compensating the CO$_2$ emissions; nevertheless the CO$_2$ emissions reduction during green sugarcane harvest made could be considered as a low carbon agricultural practice subject matter of carbon tax reduction. Fig. 3 exhibits the distribution of sugarcane residues burned and the emissions due to sugarcane burning determined in this study where it is possible to observe that the main producer states are Veracruz, Jalisco and San Luis Potosí.

In addition that sugarcane burning represents a health risk for workers and the nearby population and contributes with global warming emissions, in 2015, Mexico presented its Intended Nationally Determined Contributions (INDCs) in the Paris Conference of Parties (COP 21) with a commitment reduction of 22% of GHG and 51% of

Table 8
Emission factors of PAHs in TSP (g kg^{-1} dry fuel) from sugarcane burning.

PAHs in particles	ng m^{-3} n = 3	EF mg kg^{-1} n = 3	EF mg kg^{-1} Hall et al., 2012
Naphthalene (NAPH)	1361.20 ± 91.93	0.414 ± 0.087	4.83 ± 0.72[b]
2-Methylnaphthalene (2MNAP)	154.61 ± 18.87	0.005 ± 0.001	ND
Acenaphthylene (ACY)	34.19 ± 12.09	0.001 ± 0.001	0.78 ± 0.09[b]
Acenaphthene (ACE)	33.75 ± 5.23	0.001 ± 0.000	ND
Fluorene (FLU)	ND	ND	0.26 ± 0.05[b]
Phenanthrene (PHE)	283.29 ± 20.47	0.009 ± 0.001	0.73 ± 0.10[b]
Anthracene (ANT)	36.88 ± 3.19	0.001 ± 0.000	0.14 ± 0.03[b]
Fluoranthene (FLT)	309.30 ± 36.64	0.010 ± 0.002	0.20 ± 0.02[b]
Pyrene (PYR)	234.62 ± 11.52	0.007 ± 0.001	0.18 ± 0.01[b]
Retene (RET)	2.17 ± 0.71	< 0.0001	ND
Benzo[a]Anthracene (BAA)	858.85 ± 76.05	0.026 ± 0.009	ND
Chrysene (CRY)	1202.04 ± 74.03	0.037 ± 0.008	ND
Benzo[*b*]fluoranthene (BBF)	8599.89 ± 448.25	0.265 ± 0.04	ND
Benzo[*k*]fluoranthene (BKF)	8579.49 ± 439.02	0.264 ± 0.08	ND
Benzo[*a*]pyrene (BAP)	8265.80 ± 369.12	0.254 ± 0.015	ND
Perylene (PER)	1130.98 ± 72.15	0.035 ± 0.011	ND
Indeno[*123-cd*]pyrene (IND)	6073.44 ± 782.43	0.187 ± 0.032	ND
Dibenzo[*ah*]anthracene (DAA)	567.00 ± 61.27	0.017 ± 0.005	ND
Benzo[*ghi*]perylene (BGP)	4724.11 ± 179.37	0.145 ± 0.02	ND
ΣEF PAH	**42451.6**	**1.678**	

n = number of samples. Uncertainties are reported as combined uncertainty.

Table 9
Sugarcane burned in 2016–2017 harvest and emissions.

		Emissions (Mg)	
Production (Mg)[a]	53,308,643	**CO_2**	10,009,050
Fraction residue-crop product[b]	0.2	**CH_4**	14,166
Fraction of dry matter[b]	0.8954	**CO**	158,984
Fraction of residue burned[b]	0.72	**PM_{10}**	11,197
Combustion efficiency[b]	0.9	**$PM_{2.5}$**	7362
Crop residues burned (Mg)	6,186,140	**BC**	2289

[a] Conadesuca, 2017.
[b] Mugica-Álvarez, 2016.

black carbon for the year 2030 (SEMARNAT, 2015), taking 2013 as the year base. Then, the reduction or elimination of sugarcane burning emissions substituted by manual or mechanized green harvesting would represent double the benefit for the country; thus, government policy-makers should design viable strategies in conjunction with mills' owners. Additionally to application of Emission Inventories, the EFs estimated in this research can be applied to models for the study of different climatic scenarios as well as for air quality forecasting models.

On the first hand, laws should be passed to regulate and eventually eliminate agricultural burning that might be complemented with soft credits and tax benefits for low carbon agriculture. Brazil, the main producer of sugarcane in the world, currently shows a fast increase in the implementation of green cane management system based in several programs of sustainable agriculture. For instance, the government of Sao Paulo, passed a State law (11.241/2002) that establishes the complete elimination of sugarcane burning by 2021 in mechanized areas, and by 2031 in non-mechanized areas with high slopes, where almost all the mills are participating in the agreement (Capaz et al., 2013). In Mexico, the ban of sugarcane burning would represent the reduction of more than 10,025,000 Mg of climatic pollutants with a co-benefit in air quality avoiding the emission of more than 11,000 Mg of PM and more than 160,000 Mg of CO.

On the second hand, sustainable agricultural practices of residues management should be developed, promoting leaving the straw on the field as soil protection against erosion, reducing the soil moisture losses, inhibiting weed growth and improving soil nutritional balance (Capaz et al., 2013; Leal et al., 2013). Additionally, sugarcane straw has similar HHV and other characteristics to bagasse, then it could be used also as biofuel for electricity generation, nevertheless several studies should be performed relating to collection, storage, use and processing costs of sugarcane straw (Leal et al., 2013). Recently the use of whole sugarcane biomass (bagasse, straw and tops) has been recommended for the production of second-generation ethanol, thereby enhancing the economic viability of sugarcane industry (Pereira et al., 2015). In the case of agriculture for biofuel production, regulations based on lifecycle emissions could be implemented requiring that suppliers reduce average lifecycle of GHG and BC emissions (Rajagopal, 2013). Finally, investment in new technologies related to green harvesting should be developed in order to ease manual cutting and the mechanized harvesting in areas with high slopes or rocky soils.

4. Conclusions

Two different varieties of sugarcane (*Sacharium oficinarum*) residues were collected in locations with different soils and weather conditions in order to determine the emission factors of atmospheric and climatic pollutants from sugarcane burning using a standardized U.S. EPA, 2017 in a constructed burner that simulates such burning. It was found that biomass feeding should be done in batches to simulate adequately flaming and smoldering stages during sugarcane burning, and that EFs

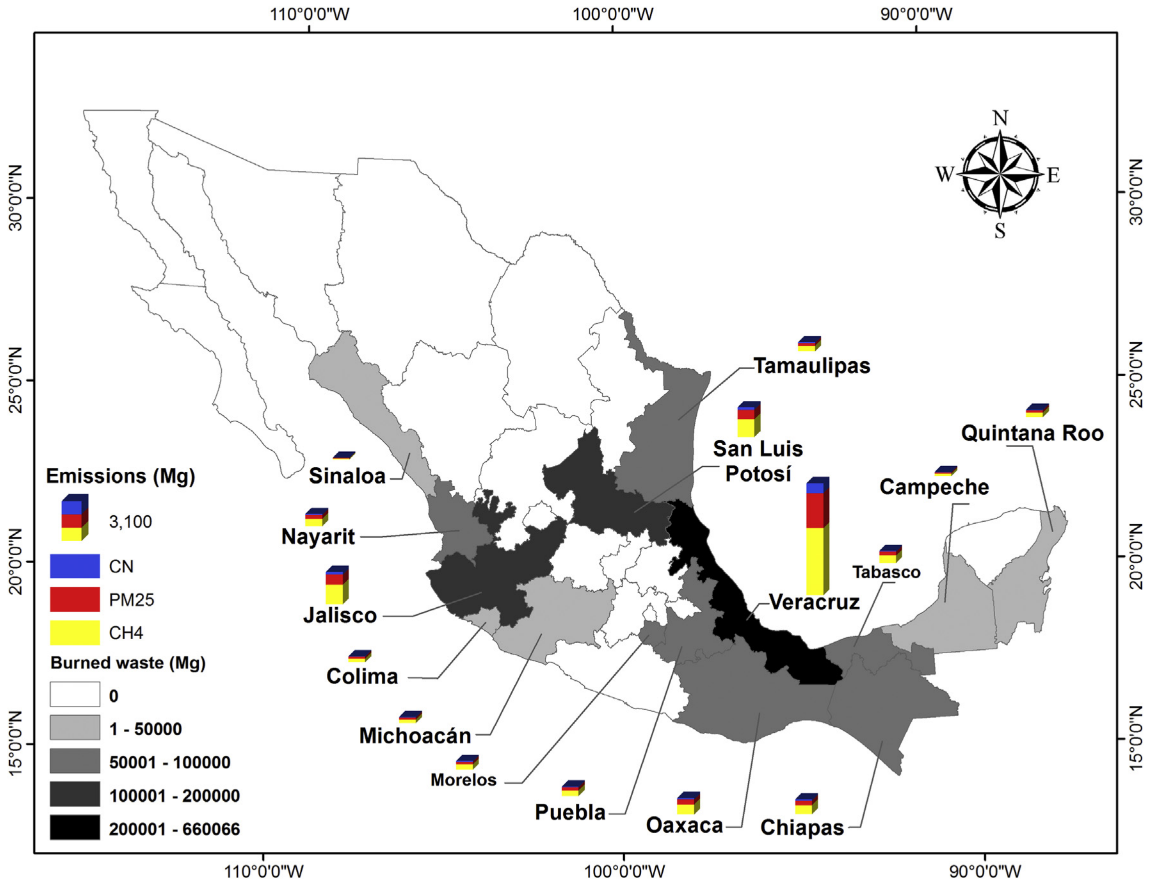


Fig. 3. Distribution of sugarcane residues production and emissions from burning during 2016–2017 harvesting.

are quite different when feeding becomes continuous.

Average values of emission factors of CO_2, CO, CH_4, PM_{10}, $PM_{2.5}$, were 1618 ± 108, 5.7 ± 2.04, 2.29 ± 0.13, 1.81 ± 0.14 and 1.19 ± 0.08 $g\,kg^{-1}$, respectively. None of the EFs determined presented significant differences between sugarcane varieties, suggesting that they can be applied for emission estimations from sugarcane burning in sites with similar soils of or weather than México.

Emission factors of EC for PM_{10} and $PM_{2.5}$ were determined as 0.37 ± 0.10 and 0.34 ± 0.09 $g\,kg^{-1}$ respectively, whereas OC EFs were 0.67 ± 0.36 and 0.44 ± 0.13 $g\,kg^{-1}$, respectively.

Particulate matter is enriched with K and Cl^{-1}, representing around 45.5% of the $PM_{2.5}$ mass. The sum of PAHs EF was 1.679 $mg\,kg^{-1}$ and most abundant PAHs were benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, and benzo[*a*]pyrene, which is consistent with the most abundant PAHs determined in the atmosphere of towns and cities close to sugarcane fields.

EFs determined were employed to estimate Mexican emissions of climatic and atmospheric pollutants, indicating that during 2016–2017 harvesting emitted more than 10,025,000 Mg of GHG, 2280 Mg of BC and more than 170,000 Mg of atmospheric pollutants; Veracruz State is the main producing state accounting for approximately 40% of the emissions.

The results of this study show the need to establish public policies, regulations and laws to reduce and eventually eliminate the sugarcane burning practice and develop systems of residues management including the use of the sugarcane straw as biofuel.

Acknowledgments

Authors thank the support by the Mexican Climate Fund 2016 (SEMARNAT), by the National Institute of Ecology and Climate Change, Mexico, project INECC/A1-002/2016 and by the CONACYT, Mexico project number 181231. VMA thanks the stipend by the National Research System.

References

Akagi, S.K., Yokelson, R.J., Wiedinmyer, C., Alvarado, M.J., Reid, J.S., Karl, T., Crounse, J.D., Wennberg, P.O., 2011. Emission factors for open and domestic biomass burning for use in atmospheric models. Atmos. Chem. Phys. 11, 4039–4072.

Andreae, M.O., Merlet, P., 2001. Emission of trace gases and aerosols from biomass burning. Global Biogeochem. Cycles 15, 955–966.

Arbex, M.A., Martins, L.C., de Oliveira, R.C., Pereira, L.A.A., Arbex, F.F., Cançado, J.E.D., Nascimiento Saldiva, P., Braga, A.L.F., 2007. Air pollution from biomass burning and asthma hospital admissions in a sugar cane plantation area in Brazil. J. Epidemiol. Community Health 61 (5), 395–400. https://doi.org/10.1136/jech.2005.044743.

ASTM D1104-56, 1978. Method of Test for Holocellulose in Wood.

ASTM, 2000. Standard Test Method for Gross Calorific Value of Coal and Coke by the Adiabatic Bomb Calorimeter. Designation D2015-00.

Badarinath, K.V.S., Kharol, S.K., Sharma, A.R., 2009. Long-range transport of aerosols from agriculture crop residue burning in Indo-Gangetic plains a study using LIDAR, ground measurements and satellite data. J. Atmospheric Sol. Terrestial Phys. 71, 112–120.

Birch, M.E., Cary, R.A., 1996. Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust. Aerosol Sci. Technol. 25, 221–241.

Bond, T.C., Doherty, S.J., Fahey, D.W., Forster, P.M., Berntsen, T., DeAngelo, B.J., Flanner, M.G., Ghan, S., Kärcher, B., Koch, D., Kinne, S., Kondo, Y., Quinn, P.K., Sarofim, M.C., Schultz, M.G., Schulz, M., Venkataraman, C., Zhang, H., Zhang, S., Bellouin, N., Guttikunda, S.K., Hopke, P.K., Jacobson, M.Z., Kaiser, J.W., Klimont, Z., Lohmann, U., Schwarz, J.P., Shindell, D., Storelvmo, T., Warren, S.G., Zender, C.S., 2013. Bounding the role of black carbon in the climate system: a scientific assessment. J. Geophys. Res. Atmospheres. 118 5380–5552.

Cançado, J.E.D., Saldiva, P.H.N., Pereira, L.A.A., Lara, L.B.L.S., Artaxo, P., Martinelli, L.A., Arbex, M.A., Zanobetti, A., Braga, A.L.F., 2006. The impact of sugarcane burning emissions on the respiratory system of children and elderly. Environ. Health Perspect. 114, 725–729.

Capaz, R.S., Carvalho, C.V.B., Nogueira, L.A.H., 2013. Impact of mechanization and previous burning reduction on GHG emissions of sugarcane harvesting operations in Brazil. Appl. Energy 102 (2), 220–228.

Cárdenas, D.M.R., Vela, H.S., Quinche, J.E.P., 2014. Estimación de hidrocarburos aromáticos policíclicos y metales pesados asociados con la quema de caña de azúcar en el valle geográfico del río Cauca, Colombia. Épsilon (21), 57–82.

Chen, J., Li, C., Ristovski, Z., Milic, A., Gu, Y., Islam, M., Wang, S., Hao, J., Zhang, H., He, C., Guo, H., Fu, H., Miljevic, B., Morawska, L., Thai, P., Lam, Y.F., Pereira, G., Ding, A., Huang, X., Dumka, U., 2017. A review of biomass burning: emissions and impacts on air quality, health and climate in China. Sci. Total Environ. 579, 1000–1034.

Chung, C.E., Ramanathan, V., Decremera, D., 2012. Observationally constrained estimates of carbonaceous aerosol radiative forcing. Proc. Natl. Acad. Sci. U.S.A. 109 (29) 11624-1162.

Conadesuca, 2017. Cosecha de caña de azúcar en estado verde en Boletín técnico informativo.

Cristale, J., Silva, F.S., Zocolo, G.J., Marchi, M.R.R., 2012. Influence of sugarcane burning on indoor/outdoor PAH air pollution in Brazil. Environ. Pollut. 169, 210–216.

Crowe, J., Wesseling, C., Román Solano, B., et al., 2013. Heat exposure in sugarcane harvesters in Costa Rica. Am. J. Ind. Med. 56 (10), 1157–1164.

Crutzen, P.J., Andreae, M.O., 1990. Biomass burning in the topics: impact on atmospheric chemistry and biogeochemical cycles. Science 250, 1669–1678.

Darley, E.F., 1974. Air Pollution Emissions from Burning Sugarcane and Pineapple from Hawai. Amendmend to EPA Research Grant R800711, Air Pollution from Forest and Agricultural Burning. Stadewide Air Pollution Research Center, University of California, Riverside August 1975.

Das, P., Ganesh, A., Wangikar, P., 2004. Influence of pretreatment for deashing of sugarcane bagasse on pyrolysis products. Biomass Bioenergy 27, 445–457.

De Andrade, S.J., Cristale, J., Silva, F.S., Julião Zocolo, G., Marchi, M.R.R., 2010. Contribution of sugar-cane harvesting season to atmospheric contamination by polycyclic aromatic hydrocarbons (PAHs) in Araraquara city, Southeast Brazil. Atmos. Environ. 44, 2913–2919.

De Oliveira Alves, N., de Souza Hacon, S., De Oliveira Galvão, M.F., Simoes Peixoto, M., Artaxo, P., de Castro Vasconcellos, P., de Medeiros, S.R.B., 2014. Genetic damage of organic matter in the Brazilian Amazon: a comparative study between intense and moderate biomass burning. Environ. Res. 130, 51–58.

De Oliveira Galvão, M.F., de Oliveira Alves, N., Ferreira, P.A., Caumo, S., de Castro Vasconcellos, P., Artaxo, P., de Souza Hacon, S., Roubicek, D.A., Batistuzzo de Medeiros, S.R., 2018. Biomass burning particles in the Brazilian Amazon region: mutagenic effects of nitro and oxy-PAHs and assessment of health risks. Environ. Pollut. 233, 260–270.

de França, D.A., Longo, K.M., Neto, T.G.S., Santos, J.C., Freitas, S.R., Rudorff, B.F.T., Cortez, E.V., Anselmo, E., Carvalho, J.A., 2012. Pre-harvest sugarcane burning: determination of emission factors through laboratory measurements. Atmosphere 3, 164–180.

Fitzpatrick, E.M., Ross, A., Bates, J., Andrews, J., Phylaktou, H., Pourkashanian, M., Williams, A., 2007. Emission of oxygenated species from the combustion of pine wood and its relation to soot formation. Process Saf. Environ. Protect. 85, 430–440.

García, C.A., Fuentes, A., Hennecke, A., Riegelhaupt, E., Manzini, F., Masera, O., 2011. Lifecycle greenhouse gas emissions and energy balances of sugarcane ethanol production in Mexico. Appl. Energy 88, 2088–2097.

Garzón, J.P., Huertas, J.I., Magaña, M., Huertas, M.E., Cárdenas, B., Watanabe, T., 2015. Volatile organic compounds in the atmosphere of Mexico City. Atmos. Environ. 119, 415–429.

Godoi, A.F.L., Ravindra, K., Godoi, R.H.M., Andrade, S.J., Santiago-Silva, M., Van Vaeck, L., Van Grieken, R.J., 2004. Fast chromatographic determination of polycyclic aromatic hydrocarbons in aerosol samples from sugar-cane burning. J. Chromatogr. A 1027, 49–53.

Goodarzi, 2006. The rates of emissions of fine particles from some Canadian coal-fired power plants. Fuel 85, 425–433.

Hall, D., Wu, C.-Y., Hsu, Y.-M., Stormer, J., Engling, G., Capeto, K., Wang, J., Brown, S., Li, H.-W., Yu, K.-M., 2012. PAHs, carbonyls, VOCs and $PM_{2.5}$ emission factors for preharvest burning of Florida sugarcane. Atmos. Environ. 55, 164–172.

Hays, M.D., Fine, P.M., Geron, C.D., Kleeman, M.J., Gullett, B.K., 2005. Open burning of agricultural biomass: physical and chemical properties of particle-phase emissions. Atmos. Environ. 39, 6747–6764.

Hedberg, E., Kristensson, A., Ohlson, M., Johansson, C., Johansson, P.-Å., Swietlicki, E., Vesely, V., Wideqvist, U., Westerholm, R., 2002. Chemical and physical characterization of emissions from birch wood combustion in a wood stove. Atmos. Environ. 36, 4823–4837.

IPCC, 1996. Guidelines for National Greenhouse Gas Inventories.

ISO 23210, 2009. Stationary Source Emissions. Determination of PM10/PM2.5 Mass Concentration in Flue Gas Measurement at Low Concentrations by Use of Impactors.

Jenkins, B.M., Jones, A.D., Turn, S.Q., Williams, R.B., 1996. Emission factors for polycyclic aromatic hydrocarbons from biomass burning. Environ. Sci. Technol. 30, 2462–2469.

Kaufman, Y.J., Didier, T., Olivier, B., 2002. A satellite view of aerosols in the climate system. Nature 419, 215–223.

Khan, A.A., Jong, W., Jansens, P.J., Spliethoff, H., 2009. Biomass combustion in fluidized bed boilers: potential problems and remedies. Fuel Process. Technol. 90, 21–50.

Koppmann, R., von Czapiewski, K., Reid, J.S., 2005. A review of biomass burning emissions, part I: gaseous emissions of carbon monoxide, methane, volatile organic compounds, and nitrogen containing. compounds. Atmos. Chem. Phys. Discuss. 2005, 10455–10516.

Kristensson, A., Johansson, C., Westerholm, R., Swietlicki, E., Gidhagen, L., Wideqvist, U., Vesely, V., 2004. Real-world traffic emission factors of gases and particles measured in a road tunnel in Stockholm, Sweden. Atmos. Environ. 38 (5), 657–673.

Kurschner, K., Hoffer, A., 1993. Cellulose and cellulose derivate. Fresenius' J. Anal. Chem. 92 (3), 145–154.

Lamminen, E., 2010. Simultaneous PM_{10} and $PM_{2.5}$ Measurement from Stacks According to New ISO 23210 Standard. Dekati Ltd. Tampere, Finland.

Leal, M., Galdos, M.V., Scarpare, F.V., Seabra, J.E.A., Walter, A., Oliveira, C.O.F., 2013. Sugarcane straw availability, recovery and energy use: a literature review. Biomass Bioenergy 53, 11–19.

Mc Meeking, G.R., Kreidenweis, S.M., Baker, S., Carrico, C.M., Chow, J.C., Collett, J.L., Hao, W.M., Holden, A.S., Kirchstetter, T.W., Malm, W.C., Moosmüller, H., Sullivan, A.P., Wold, C.E., 2009. Emissions of trace gases and aerosols during the open combustion of biomass in the laboratory. J. Geophys. Res. 114 D19210.

Mugica, V., Hernández, S., Torres, M., García, R., 2010. Seasonal variation of polycyclic aromatic hydrocarbons exposure levels in Mexico City. J. Air Waste Manage. Assoc. 60, 548–555.

Mugica-Álvarez, V., Santiago-De La Rosa, N., Figueroa-Lara, J., Flores-Rodríguez, J., Torres-Rodríguez, M., Magaña-Reyes, M., 2015. Emissions of PAHs derived from sugarcane burning and processing in Chiapas and Morelos México. Sci. Total Environ. 527–528, 474–482.

Mugica-Álvarez, V., 2016. Final report of the project INECC/A1-002, 2016: Determinación de factores de emisión de bióxido de carbono (CO_2), partículas en suspensión de 2.5 y 10 micras ($PM_{2.5}$ y PM_{10}) y contaminantes de vida corta, metano (CH_4) y carbono negro por prácticas de quema agrícola. (México).

Mugica-Alvarez, V., Hernández-Moreno, A., Valle-Hernández, B.L., Millán-Vázquez, F., Espejo-Montes, F., Torres-Rodríguez, M., 2017. Characterization and modelling of atmospheric particles from sugarcane burning in Morelos, Mexico. Hum. Ecol. Risk Assess. 23, 1056–1071.

Murillo, J.H., Rojas Marín, J.F., Mugica Álvarez, V., Solórzano Arias, D., Guerrero, V.H.B., 2017. Chemical characterization of filterable $PM_{2.5}$ emissions generated from regulated stationary sources in the metropolitan area of Costa Rica. Atmos. Pollut. Res. 8, 709–717.

NEI-EPA, 2014. National Emission Inventories Documentation. Consulted 03-01-2018. www.epa.gov/air-emissions-inventories/2014-national-emissions-inventory-nei-documentation.

Neto, T.G., Carvalho Jr., J.A., Cortez, E.V., Azevedo, R.G., Oliveira, R.A., Fidalgo, W.R.R., Santos, J.C., 2011. Laboratory evaluation of Amazon forest biomass burning emissions. Atmos. Environ. 45, 7455–7461.

Pereira, S.C., Maehara, L., Machado, C.M.M., Farinas, C.S., 2015. 2G ethanol from the whole sugarcane lignocellulosic biomass. Biotechnol. Biofuels 8, 44.

Petzold, A., Ogren, J.A., Fiebig, M., Laj, P., Li, S.-M., Baltensperger, U., Holzer-Popp, T., Kinne, S., Pappalardo, G., Sugimoto, N., Wehrli, C., Wiedensohler, A., Zhang, X.-Y., 2013. Recommendations for reporting “black carbon” measurements. Atmos. Chem. Phys. 13, 8365–8379.

Prado, G.F., Zanetta, D.M., Arbex, M.A., Braga, A.L., Pereira, L.A., de Marchi, M.R., de Melo Loureiro, A.P., Marcourakis, T., Sugauara, L.E., Gattás, G.J., Gonçalves, F.T., Salge, J.M., Terra-Filho, M., de Paula Santos, U., 2012. Burnt sugarcane harvest-ing: particulate matter exposure and the effects on lung function, oxidative stress, and urinary 1-hydroxypyrene. Sci. Total Environ. 437, 200–208.

Rajagopal, D., 2013. The fuel market effects of biofuel policies and implications for regulations based on lifecycle emissions. Environ. Res. Lett. 8, 024013.

Ramanathan, V., Carmichael, G.R., 2008. Global and regional climate changes due to black carbon. Nat. Geosci. Lett. 221–227.

Ravindra, K., Sokhi, R., Grieken, R.V., 2008. Atmospheric polycyclic aromatic hydrocarbons: source attribution, emission factors and regulation. Atmos. Environ. 42, 2895–2921.

Sanchis, E., Ferrer, M., Calvet, S., Coscollà, C., Yusà, V., Cambra-López, M., 2014. Gaseous and particulate emission profiles during controlled rice straw burning. Atmos. Environ. 98, 25–31.

Santiago-De La Rosa, N., González-Cardoso, G., Figueroa-Lara, J.J., Gutiérrez-Arzaluz, M., Octaviano-Villasana, C., Ramírez-Hernández, I.F., Mugica-Álvarez, V., 2018. Emission factors of atmospheric and climatic pollutants from crop residues burning. J. Air and Waste Manag. https://doi.org/10.1080/10962247.2018.1459326.

Santos, U.P., Zanetta, D.M., Terra-Filho, M., Burdmann, E., 2015. Burnt sugarcane harvesting is associated with acute renal dysfunction. Kidney Int. 87, 792–799.

SEMARNAT, 2015. Intended Nationally Determied Contribution.

Sevimoglu, O., Rogge, W.R., 2015. Organic compound concentrations of size-segregated PM10 during sugarcane burning and growing seasons at a rural and an urban site in Florida, USA. Aerosol and Air Quality Research 15, 1720–1736.

Silva, F.S., Cristale, J., André, P.A., Saldiva, P.H.N., Marchi, M.R.R., 2010. PM2.5 and PM10: the influence of sugarcane burning on potential cancer risk. Atmos. Environ. 44, 5133–5138.

Silveira, H., Schmidt-Carrijo, M., Seidel, E.H., Scapulatempo-Neto, C., Longatto-Filho, A., Lopes-Carvalho, A., Vieira-Reis, R., Saldivas, P.H., 2013. Emissions generated by sugarcane burning promote genotoxicity in rural workers: a case study in Barretos, Brazil. Environ. Health 12, 87.

Singh, Y., Sidhu, H.S., 2014. Management of cereal crop residues for sustainable rice-wheat production system in the Indo-Gangetic plains of India. Proc. Indian Nat. Sci. Acad. 80, 95–114.

Stirling, G.R., Moody, P.W., Stirling, A.M., 2010. The impact of an improved sugarcane farming system on chemical, biochemical and biological properties associated with soil health. Appl. Soil Ecol. 46, 470–477.

Stockwell, C.E., Yokelson, R.J., Kreidenweis, S.M., Robinson, A.L., DeMott, P.J., Sullivan, R.C., Reardon, J., Ryan, K.C., Griffith, D.W.T., Stevens, L., 2014. Trace gas emissions from combustion of peat, crop residue, domestic biofuels, grasses, and other fuels: configuration and Fourier transform infrared (FTIR) component of the fourth Fire Lab at Missoula Experiment (FLAME-4). Atmos. Chem. Phys. 14, 9727–9754.

T222 OM-02, 2006. Acid-insoluble Lignin in Wood and Pulp.

TAPPI T204 cm-97, 2007. Solvent Extractives of Wood and Pulp.

Tissari, J., Lyyränen, J., Hytönen, K., Sippula, O., Tapper, U., Frey, A., Saarnio, K., Pennanen, A.S., Hillamo, R., Salonen, R.O., Hirvonen, M.-R., Jokiniemi, J., 2008. Fine particle and gaseous emissions from normal and smouldering wood combustion in a conventional masonry heater. Atmos. Environ. 42, 7862–7873.

Tsai, W.T., Lee, M.K., Chang, Y.M., 2006. Fast pyrolysis of rice straw, sugarcane bagasse and coconut shell in an induction-heating reactor. J. Anal. Appl. Pyrolysis 76, 230–237.

Tsiouri, V., Kakosimos, K.E., Kumar, P., 2015. Concentrations, sources and exposure risks associated with particulate matter in the Middle East Area—a review. Air Qual Atmos Health 8, 67.

UNEP and WMO, 2011. Integrated Assessment of Black Carbon and Tropospheric Ozone. United Nations Environment Programme (UNEP), Nairobi, Kenya 303 pp.

UNE-EN 14774-1, 2010. Solid Biofuels - Determination of Moisture Content - Oven.

Uriarte, M., Yackulic, C.B., Cooper, T., Flynn, D., Cortes, M., Crk, T., Cullman, G., McGinty, M., Sircely, J., 2009. Expansion of sugarcane production in Sao Paulo, Brazil: implications for fire occurrence and respiratory health. Agric. Ecosyst. Environ. 132, 48–56.

U.S. EPA, 1992. fifth ed. AP-42. Open Burning, vol. I (Chapter 2): Solid Waste Disposal.

U.S. EPA, (U.S. Environment Protection Agency), 1999a. Compendium Method TO-13. Determination of Polycyclic Aromatic Hydrocarbons in Ambient Air Using Gas Chromatographic Mass Spectrometry (GC-MS).

U.S. EPA, (U.S. Environment Protection Agency), 1999b. Compendium Method TO-14 A. Determination of Volatile Organic Compounds (VOCs) in Ambient Air Using Specially Prepared Canisters with Subsequent Analysis by Gas Chromatography.

U.S. EPA, (U.S. Environment Protection Agency). Method 201 A. Determination of PM10 and PM2.5 emissions from stationary sources. Accessed 12-4-2017. https://www.epa.gov/sites/production/files/2018-03/documents/method201a1.pdf.

Valle-Hernández, B.L., Mugica-Álvarez, V., Salinas-Talavera, E., Amador-Muñoz, O., Murillo-Tovar, M.A., Villalobos-Pietrini, R., De Vizcaya-RuízA, 2010. Temporal variation of nitro-polycyclic aromatic hydrocarbons in PM_{10} and $PM_{2.5}$ collected in Northern Mexico City. Sci. Total Environ. 408, 5429–5438.

Ward, D.E., Radke, L.E., 1993. Emissions measurements from vegetation fires: a comparative evaluation of methods and results. In: Crutzen, P.J., Goldammer, J.G. (Eds.), Fire in the Environment: the Ecological, Atmospheric, and Climatic Importance of Vegetation Fires. Dahlem Workshop Reports: Environmental Sciences Research Report 13. John Wiley & Sons, Chischester, England.

Yokelson, R.J., Christian, T.J., Karl, T.G., Guenther, A., 2008. The tropical forest and fire emissions experiment: laboratory fire measurements and synthesis of campaign data. Atmos. Chem. Phys. 8, 3509–3527.

Zhang, Y., Shao, M., Lin, Y., Luan, S., Mao, N., Chen, W., Wang, M., 2013. Emission inventory of carbonaceous pollutants from biomass burning in the Pearl River Delta Region, China. Atmos. Environ. 76, 189–199.