PAHs, carbonyls, VOCs and PM$_{2.5}$ emission factors for pre-harvest burning of Florida sugarcane

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ABSTRACT

Emission factors (EFs) for hazardous polycyclic aromatic hydrocarbons (PAHs), carbonyls, and volatile organic compounds (VOCs) as well as other species such as PM$_{2.5}$, elemental carbon (EC), organic carbon (OC), and tracer compounds (e.g., levoglucosan (LG) and other sugars) were investigated for sugarcane pre-harvest burning in Florida. A combustion chamber was used to simulate field burning conditions for determining EFs of both dry leaf and whole stalk biomass burning. Samples were collected from the chamber's exhaust duct following EPA sampling methods. The total PAH EFs were 7.13 ± 0.94 and 8.18 ± 3.26 mg kg^{-1} for dry leaf and whole sugarcane stalk burning, respectively. Carbonyl EFs were 201 ± 39 and 942 ± 539 mg kg^{-1} for dry leaf and whole stalk burning, respectively. PAH and carbonyl emissions were dominated by lower molecular weight compounds (e.g., naphthalene and formaldehyde, respectively). Of the aromatic VOCs studied, benzene was the predominant species. The PM$_{2.5}$ EF was 2.49 ± 0.66 g kg^{-1}, which is in range of the current published AP-42 EFs for particulate matter emissions from sugarcane burning and other sugarcane studies. The OC, EC and LG EFs were 0.16 ± 0.09 g kg^{-1}, 0.71 ± 0.22 g kg^{-1}, and 7.87 ± 5.42 mg kg^{-1}, respectively. EFs of gaseous pollutants were generally lower than EFs from studies of agricultural residue combustion, likely due to the high combustion efficiency observed in this study.

1. Introduction

Prescribed burning of sugarcane fields is practiced to facilitate harvesting by quickly and cheaply removing excess biomass, to reduce dangers from snakes and insects (Gullett et al., 2006), and to increase the sugar content of the stalk by water evaporation (Zamperlini et al., 2000). Current emission factors (EFs) for sugarcane pre-harvest burning, published by the United States Environmental Protection Agency (US EPA) in AP-42, are currently rated as unreliable ("category D") and are only available for total particulate matter, carbon monoxide (CO), and total hydrocarbons (USEPA, 1995). The current EFs are based on one study of Hawaiian sugarcane and it is possible that the EFs of other types of sugarcane may differ (Gullett et al., 2006). Additionally, there are no compound-specific EFs for hazardous air pollutants (HAPs) such as PAHs, VOCs, or carbonyls.

In Brazil, numerous studies have been conducted on the environmental impacts of sugarcane burning. Lara et al. (2005) used principal component analysis (PCA) to study the properties of aerosols from sugarcane burning and to assess their contribution to ambient particle concentrations in Piracicaba, Brazil. They concluded that sugarcane fires were the largest source of particulate matter in the area—specifically, 60% of the fine mode (PM$_{2.5}$) mass and 25% of the coarse mode (PM$_{10-2.5}$) mass. Kirchhoff et al. (1991) also observed elevated ambient CO and ozone (O$_3$) concentrations during sugarcane burning periods in Sao Paulo, Brazil.

Gullett et al. (2006) investigated the EFs of polychlorinated dibenzodioxins and dibenzofurans (PCDD/Fs) from Floridian and Hawaiian sugarcane burning in a combustion chamber. They found Hawaiian sugarcane EFs to be over 10 times higher than Florida sugarcane EFs. One proposed explanation for the difference was the

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significantly higher (13 times) chlorine content of the Hawaiian sugarcane. Meyer et al. (2004) also studied the EFs of PCDDs and PCDFs from Australian sugarcane in the field and in a combustion chamber. Meyer's results were comparable to the EFs from Gullett's research for Florida sugarcane. The differences between these two studies highlight the important effects of biomass source and burning conditions on pollutant EFs.

The objective of this study was to develop EFs for specific hazardous air pollutants (PAHs, carbonyls and VOCs) and $PM_{2.5}$ from sugarcane burning using a combustion chamber that simulated field burning. In addition to HAPs, elemental carbon (EC), organic carbon (OC) and several tracer compounds (levoglucosan, mannosan, galactosan, xylitol, xylose) were also investigated, which can be useful for developing source profiles for source apportionment studies and source impact assessment.

2. Methodology

Fig. 1 shows a schematic of an open burning combustion chamber built to simulate field burning. The chamber consisted of a cylindrical combustion section ($\sim$0.9 m^3) where the sugarcane was burned, a cone ($\sim$0.27 m^3) to funnel the exhaust gas from the combustion section to the exhaust stack, and a stack (diameter = 20 cm) where the exhaust gas was sampled. The floor of the combustion chamber consisted of an open grid that ensured adequate air availability for the combustion process. The chamber and stack surfaces were lined with aluminum foil to prevent catalytic formation of PAHs, which is associated with steel materials (Jenkins et al., 1996b).

To enhance mixing of the combustion gases before sampling, two baffles made of aluminum were placed at the entrance of the stack. Samples were collected from the stack approximately 8.5 duct diameters (i.e., 1.7 m) downstream of the baffles (USEPA, 2000a; USEPA, 2000c). A draft inducer was employed near the exit of the stack to stabilize the pressure as well as induce excess air into the chamber.

Sugarcane biomass was obtained from Florida fields in Belle Glade and Citra, FL and all collected biomass was treated and stored in a consistent manner. Most experiments used solely dry sugarcane leaves, which were fed into the chamber at a rate of approximately 100 g every 40 s to maintain near constant burning conditions. A few experiments were conducted using whole sugarcane stalks, which contained both dry and green leaves (with higher moisture contents), to investigate the effects of biomass composition and burning conditions on the EFs. When burning whole stalks, burning conditions were highly variable both during the experiment and across experiments due to the heterogeneous nature of the biomass.

Due to limitations in space, only one pollutant was sampled per experiment. Temperature and pressure were measured in the stack at regular time intervals in order to calculate the stack velocity and flowrate following EPA Method 2 (USEPA, 2000c). Temperature was monitored using a thermocouple, and the differential pressure was measured using an s-type pitot tube. Flue gases were monitored in select experiments to evaluate the combustion conditions of the chamber. Since pollutants form through incomplete combustion, the combustion efficiency (CE) is an important parameter to monitor when investigating emissions. To evaluate the combustion conditions of the experimental system, CO, CO_2, and O_2 concentrations were measured using a CO analyzer (48C, Thermo Electron Corporation), a CO_2 Analyzer (1400, Servomex) and an O_2 analyzer (Rapidox 3000, Cambridge Sensotec) in select experiments.

2.1. PAHs

PAH sampling and analysis was based on EPA Method TO-13A (USEPA, 1999a) adapted for stack sampling. Three experiments using solely dry leaves and two using whole stalks with a mixture
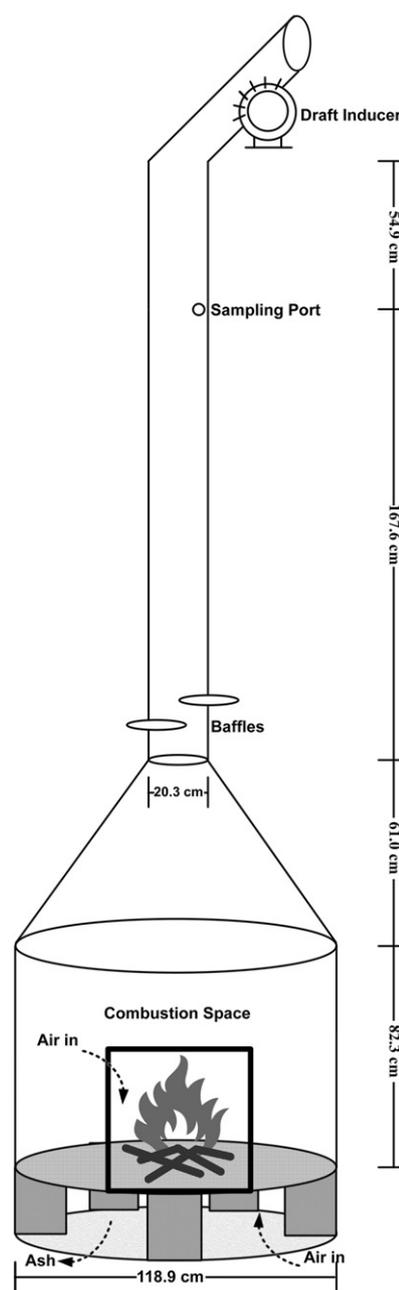

Fig. 1. Schematic of the combustion chamber.

of dry and green leaves were conducted. Two experiments collected duplicate samples; therefore, seven PAH samples were collected in total. Sampling times ranged from 30 to 70 min. On average, 4.5 kg of biomass was burned in dry leaf experiments and 8.8 kg in whole stalk experiments. Exhaust air was drawn isokinetically from the stack and passed through a quartz filter to collect particulate PAHs and then through a sorbent cartridge containing polyurethane foam (PUF) and XAD-2 resin to collect semivolatile organic compounds (SVOCs). Samples were sent to Columbia Analytical Services where they were Soxhlet extracted in a mixture of 10% diethyl ether in hexane, concentrated, and analyzed by gas chromatography–mass spectrometry (GC–MS) in accordance with EPA Method TO-13A (USEPA, 1999a). Method reporting limits (MRLs) ranged from 9.0 to 16 µg m^{-3} for naphthalene and 0.9 to 7.5 µg m^{-3} for all other PAH compounds.

2.2. Carbonyls

Carbonyl sampling and analysis followed EPA Method TO-11A (USEPA, 1999b) adapted for stack sampling. Five experiments were conducted—three for dry leaves and two for whole stalk biomass. Parallel duplicate samples were collected in four out of five experiments. Sample times ranged from three to ten minutes. On average, approximately 1 kg of biomass was burned in experiments, except one experiment where approximately 250 g was burned. Cartridges precoated with 2,4-dinitrophenylhydrazine (DNPH) (Supelco) were used to sample carbonyls. An LpDNPH ozone scrubber (Supelco) was applied to remove the interference of ozone during sampling. Following sampling, cartridges were shipped to Columbia Analytical Services where they were eluted with acetonitrile and analyzed by isocratic reverse-phase high-performance liquid chromatography (HPLC). All sample extraction and analysis procedures were performed in accordance with EPA Method TO-11A (USEPA, 1999b). MRLs ranged from 13 to 140 $\mu g\,m^{-3}$ for target compounds.

2.3. VOCs

EPA Method 18 was applied for the sampling of VOCs (USEPA, 2000b). Gas samples were collected in Tedlar bags using a Vac-U-Chamber Kit (SKC). Four experiments were conducted for VOC sampling for dry leaves. Sampling time was approximately three minutes and 300 g of biomass was burned. Samples were analyzed by GC–MS for benzene, toluene, o,m,p-xylenes, ethylbenzene and styrene following EPA Method TO-15 (USEPA, 1999c). The MRL for m,p-xylenes was 10 $\mu g\,m^{-3}$ and for all other target compounds was 5.0 $\mu g\,m^{-3}$.

2.4. $PM_{2.5}$

$PM_{2.5}$ sampling was based on EPA's Other Test Methods (OTM) 27 and 28 (USEPA, 2008a; USEPA, 2008b) with a few modifications to the impinger train. Exhaust gas was sampled isokinetically, passed through an in-stack, size selective cyclone (Sierra Instruments, Inc. Series 280 Cyclade™) to remove particles larger than 2.5 μm and then passed through a glass fiber filter (Type A/E, Gelman Sciences, Inc.) to collect the filterable particulate matter. In some experiments, an impinger train and Teflon filter (Zefluor, Pall Life Sciences) were added to cool the exhaust gas and collect the condensable particulate matter (CPM). Five PM sampling experiments were conducted. All experiments used dry leaves. $PM_{2.5}$ sampling times ranged from 1 to 18 min and mass loadings ranged from 0.2 to 2.4 kg.

The glass fiber filters were pre- and post-conditioned for at least 24 h for weighing. The front half of the filter holder and cyclone exit were rinsed with acetone, transferred to a pre-weighed weighing dish and also weighed as part of the filterable PM mass. For the CPM recovery, the impinger train was rinsed with deionized (DI) water, acetone, and methylene chloride. The rinses were carried out through procedures detailed in OTM 28 to determine the final CPM residue weight (USEPA, 2008b). A microbalance (Model MC 210 S, Sartorius Corp.; readability − 10 μg) was used for all weighing. Filters and dishes were weighed 3 times to determine the average mass and were repeatedly weighed at intervals of at least 6 h to ensure the weight was constant (defined as having a weight change of less than 0.5 mg).

2.5. EC and OC

Three $PM_{2.5}$ samples were collected on tissuquartz filters (Pall Life Sciences) to determine the emission factors of EC, OC and other tracer compounds. Prior to sampling, tissuquartz filters were baked at 550 °C for 12 h and allowed to cool for 12 h to remove any residual carbon in the filters. In these experiments, 0.5 kg of dry leaves was combusted and sampling times were, on average, 3.9 min.

Tissuquartz filters were sent cold to the Research Center for Environmental Changes, Academia Sinica in Taipei, Taiwan, where they were analyzed for EC and OC using a semi-continuous OCEC Carbon Aerosol Analyzer (Sunset Laboratory, Model 4) following the National Institute for Occupational Safety and Health (NIOSH) Method 5040 (NIOSH, 1999). As part of the analysis, a portion of each filter was heated at distinct intervals to 870 °C in a pure helium atmosphere to volatilize the organic carbon (OC). The sample was then cooled and re-heated at discrete intervals again up to 870 °C in a 2% oxygen in helium atmosphere to evolve the elemental carbon (EC). The evolved carbon fractions were subsequently oxidized to CO_2 which was quantified by a non-dispersive infra-red (NDIR) detector. Correction for the pyrolized OC fraction was accomplished by monitoring the transmittance of a laser beam through the sample filter.

For the determination of selected polar organic compounds, including molecular tracers for biomass burning, a 2.2 cm^2 filter punch was extracted in 2 mL of ultrapure water under ultrasonic agitation for 1 h. The extract was filtered through a syringe filter (0.45 μm, PTFE, Pall Life Sciences) to remove insoluble materials. Anhydrosugars (levoglucosan, mannosan and galactosan), sugars (xylose) and sugar alcohols (xylitol), were quantified by high-performance anion exchange chromatography (HPAEC) on a Dionex ICS-3000 system equipped with an electrochemical detector (Dionex, USA). The MRL for this method is 0.1 ng. A more detailed description of the HPAEC analysis method can be found in Engling et al. (2009).

2.6. Calculations

CE is defined as the fraction of carbon released as CO_2. In this study, the modified combustion efficiency (MCE) was determined using Equation (1), which assumes all of the carbon is released as CO or CO_2.

$$MCE = \Delta[CO_2]/(\Delta[CO_2] + \Delta[CO]) \tag{1}$$

where, $\Delta[CO]$ and $\Delta[CO_2]$ are the mass concentrations of CO and CO_2 in excess of the background. Previous studies have demonstrated that over 95% of carbon is released as CO or CO_2; therefore, it is reasonable to estimate the CE without hydrocarbons or particulate matter (Ward and Hardy, 1991; Gupta et al., 2001; Chen et al., 2007).

EFs were calculated using Equation (2) (Dhammapala et al., 2006), which assumes the chamber to be well mixed.

$$EF = (\Delta C_x \times Q_{chamber} \times t)/m_{burned} \tag{2}$$

where ΔC_x is the measured pollutant concentration above the ambient level, $Q_{chamber}$ is the flowrate through the chamber, t is the sampling time, and m_{burned} is the mass of biomass burned. In the cases where ambient concentrations were below detection limits, the background concentration was assumed to be zero for the EF calculations. All sample volumes and chamber flowrates were corrected to standard conditions (20 °C and 1 atm).

2.7. Quality assurance/quality control (QA/QC) measures

Ambient samples were obtained during each sampling campaign to determine the background concentrations of the compounds of interest. Field blank samples were also collected to ensure no contamination was introduced during sample storage and handling. Ambient and field blank samples were below analytical detection limits in all cases; therefore, the data was not blank corrected. Method blank samples were applied with each batch of samples analyzed to monitor for contamination and interferences in the analytical methods. Parallel duplicate samples were collected in select PAH, carbonyl, and VOC experiments to

Table 1
Summary of MCE, CO and CO_2 EFs.

	MCE (%)	Average [CO] (mg m^{-3})	Average [CO_2] (mg m^{-3})	CO EF (g kg^{-1})	CO_2 EF (g kg^{-1})
Present Study	98.5 ± 0.2	325	45,232	9.2 ± 3.3	1255 ± 287
AP-42[a]	NA	NA	NA	30–40	NA
Yokelson et al., 2008	97.6	NA	NA	28.3	1838

[a] USEPA, 1995.

measure the precision (as percent difference) of the sampling and analysis procedures.

For PAH analysis, a laboratory control sample (LCS) and a duplicate laboratory control sample (DLCS) were run with each batch of samples to monitor the extraction efficiency of target analytes. Additionally, isotopically labeled surrogate compounds (fluorene-d10 and pyrene-d10) were spiked onto the method blank, LCS, DLCS, and each sample as internal standards. Analyzed PAH concentrations were corrected to reflect compound specific (LCS and DLCS) and sample specific (surrogate compounds) extraction efficiencies.

For carbonyl sampling, a breakthrough test was conducted by placing two DNPH cartridges in series. The backup cartridge was analyzed to verify no sampling breakthrough occurred. Regarding VOCs, with each batch of samples analyzed, an LCS was prepared by spiking a Tedlar bag with known concentrations of the target analytes. The bag was analyzed to evaluate the analytical method's recovery. LCS recoveries for all compounds ranged from 79 to 98%. Additionally, surrogate compounds (1,2-dichloroethane-d4 and toluene-d8) were spiked into each sample analyzed to measure their recovery. Recoveries of 1,2-dichloroethane-d4 and toluene-d8 ranged from 94 to 111% and 95 to 103%, respectively. All recoveries were within the acceptable criteria of the analytical method.

A study was also conducted to determine the recovery efficiencies of target VOC compounds. A canister was spiked with compounds of known concentrations and then was sampled using the Tedlar bag and Vac-U-chamber system. The recovery efficiencies for the target compounds were, benzene: 80%, toluene: 79%, ethylbenzene: 80%, m,p-xylenes: 75%, styrene: 51%, and o-xylene: 71%. The recovery for higher molecular weight compounds, such as styrene, was rather low using this sampling method.

3. Results and discussion

3.1. Flue gases

Flue gases were monitored for three burning events where dry leaves were burned. Table 1 summarizes the average CO and CO_2 concentrations, the CO and CO_2 EFs, and the average MCE. The high MCE observed, 98.5 ± 0.21%, indicates the dominance of flaming combustion in this studied scenario.

3.2. PAHs

Species specific PAH EFs are presented in Table 2. The total PAH EF for dry leaf burning was 7.13 ± 0.94 mg kg^{-1}. Based on one sample pair, the precision was 5%. This EF does not include any emissions of higher molecular weight compounds, which were below detection limits in these experiments. The whole stalk EF was slightly higher than dry leaf experiments—8.18 ± 3.26 mg kg^{-1}. Based on one sample pair, the precision was 15%.

PAH emissions were dominated by low molecular weight compounds (i.e., two and three ring PAH compounds). In fact, naphthalene (2-ringed) contributed to 66% of the overall EF, on average. Three-ring PAHs (acenaphthylene, acenaphthene, fluorene, phenanthrene and anthracene) contributed to 27% of the total PAH EF and 4-ring PAHs (fluoranthene, pyrene, benzo[a]anthracene and chrysene) contributed to 8% of the total EF, on average.

PAH concentrations for the whole stalk burning (223–306 µg m^{-3}) were slightly higher than for dry leaf burning (119–136 µg m^{-3}). As other studies have demonstrated, moisture content (MC) has an important impact on emissions (Hays et al., 2005; McMeeking et al., 2009; Simoneit, 2002). Generally, higher MCs inhibit combustion by lowering the temperature and CE, leading to higher pollutant emissions. However, at very low moisture contents the biomass burns quickly, creating oxygen-limited conditions leading to a decrease in the CE.

In addition to CE, PAH formation is sensitive to temperature—formation is supported at high temperatures (in excess of 500 °C) (Conde et al., 2005). While higher MC fuels may exhibit lower CEs, they also likely have a lower combustion temperature, possibly inhibiting PAH formation (Korenaga et al., 2001). This may explain why whole stalk PAH EFs were only slightly higher than dry leaf EFs. It is apparent that there are

Table 2
Summary of PAH EFs (mg kg^{-1}).

	Sugarcane (present study)		Other references
	Dry leaves	Whole stalks	
Naphthalene	4.83 ± 0.72	5.24 ± 2.45	1.330–347.988[c,d]
Acenaphthylene	0.78 ± 0.09	0.80 ± 0.30	3.5[a], 6.9[b], 0.308–22.080[c]
Acenaphthene	ND	0.11	0.22[a], 0.60[b], 0.013–17.936[c]
Fluorene	0.26 ± 0.05	0.27 ± 0.20	0.83[a], 1.6[b], 0.046–3.277[c]
Phenanthrene	0.73 ± 0.10	0.87 ± 0.25	4.1[a], 4.0[b], 1.320–20.923[c]
Anthracene	0.14 ± 0.03	0.15 ± 0.06	1.4[a], 1.2[b], 0.061–3.977[c]
Fluoranthene	0.20 ± 0.02	0.30 ± 0.05	1.4[a], 1.2[b], 0.425–6.654[c]
Pyrene	0.18 ± 0.01	0.27 ± 0.05	1.3[a], 1.1[b], 0.337–5.031[c]
Benz[a]anthracene	ND	0.05 ± 0.01	0.87[a], 1.1[b], 0.060–2.276[c]
Chrysene	ND	0.08 ± 0.02	0.078–2.326[c]
Benzo[b]fluoranthene	ND	0.06 ± 0.00	0.47[a], 0.31[b], 0.018–9.311[c]
Benzo[k]fluoranthene	ND	0.03 ± 0.01	0.51[a], 0.44[b], 0.30–4.249[c]
Benzo[a]pyrene	ND	0.04 ± 0.01	0.39[a], 0.47[b], 0.006–14.336[c]
Indeno[1,2,3-cd]pyrene	ND	0.03 ± 0.00	0.032[a], 0.054[b], 0.070–4.836[c]
Benzo[g,h,i]perylene	ND	0.03 ± 0.00	0.083[a], 0.19[b], 0.001–1.046[c]

[a] Dhammapala et al. (2007), wheat.
[b] Dhammapala et al. (2007), Kentucky bluegrass.
[c] Jenkins et al. (1996b), agricultural and forest biomass.
[d] Data flagged as questionable by Jenkins et al. (1996b).

numerous factors that impact emissions and these relationships are not always straightforward.

As naphthalene consistently comprises a large portion of the PAH emissions, it serves as a good indicator of the total PAH concentration. Conde et al. (2005) found a strong relationship between the total PAH concentration and the naphthalene concentration. Naphthalene is one of the first PAH compounds formed and is one of the most stable. It also serves as a building block for further PAH formation, making it a good indicator of total PAH formation (Conde et al., 2005). In the present study, strong relationships were found between naphthalene, acenaphthylene, and phenanthrene concentrations and the total PAH concentration, as summarized in Fig. 2. The results suggest that measuring a few select PAH compounds could infer the total PAH emissions from a particular source.

Table 2 compares the sugarcane EFs to different agricultural residues from other studies. Sugarcane EFs are comparable, but are generally lower than EFs published for other agricultural materials. The relative abundance of acenaphthylene and phenanthrene is consistent for all fuel types. It addition to the obvious difference of fuel type, the lower EFs exhibited in this study can be attributed to the high MCE observed in this study ($\sim$99%).

3.3. Carbonyls

Five experiments were performed for carbonyl sampling—3 for dry leaves and 2 for whole sugarcane stalks. The mean total carbonyl EFs were 202 ± 39 mg kg^{-1} (average 25% precision based on 2 sample pairs) and 942 ± 539 mg kg^{-1} (average 11% precision based on 2 sample pairs) for dry leaf and whole stalk burnings, respectively. Table 3 summarizes the compound specific carbonyl EFs as well as carbonyl EFs from other studies. In all experiments, formaldehyde was the most dominant carbonyl compound accounting for over 50% (ranging 51–78%) of quantified carbonyl emissions. Acetaldehyde was the second most abundant compound followed by propionaldehyde.

As with the dominant PAH compounds, formaldehyde and acetaldehyde concentrations were highly correlated with the total carbonyl concentrations. Fig. 3 shows the correlations between formaldehyde and acetaldehyde concentrations and the total carbonyl concentration. Because of their strong correlation, formaldehyde and acetaldehyde could serve as predictor compounds for total carbonyl emissions.

Whole stalk burning exhibited considerably higher EFs than dry leaf experiments for all compounds except valeraldehyde. The ratio of whole stalk EFs to dry stalk EFs ranged from 0.8 (valeraldehyde) to 7.2 (acetaldehyde). The higher EFs from whole stalk experiments can be partially attributed to the high moisture content of the fuel. Whole stalk experiments also exhibited higher EF variability between experiments, which can be attributed to variable burning conditions and differences in the biomass source. Significant differences in the burning conditions were observed during the two whole stalk experiments. The first fire was much more intense—the average stack temperature was 315 °C and 1 kg of biomass burned in 3 min, whereas in the later experiment only 253 g of biomass burned in 3 min and the average temperature was around 63 °C. The different burning conditions were a result of different initial loading conditions and operator differences. The variation in the EFs can be attributed to these differences in burning conditions. The more intense fire was characterized by more flaming combustion as compared to the lower temperature fire, which exhibited more smoldering combustion. Therefore, in addition to the differences in burning conditions and MC, the biomass composition, condition, and treatment practices (which differed for the different growing areas) may have also influenced the EFs.
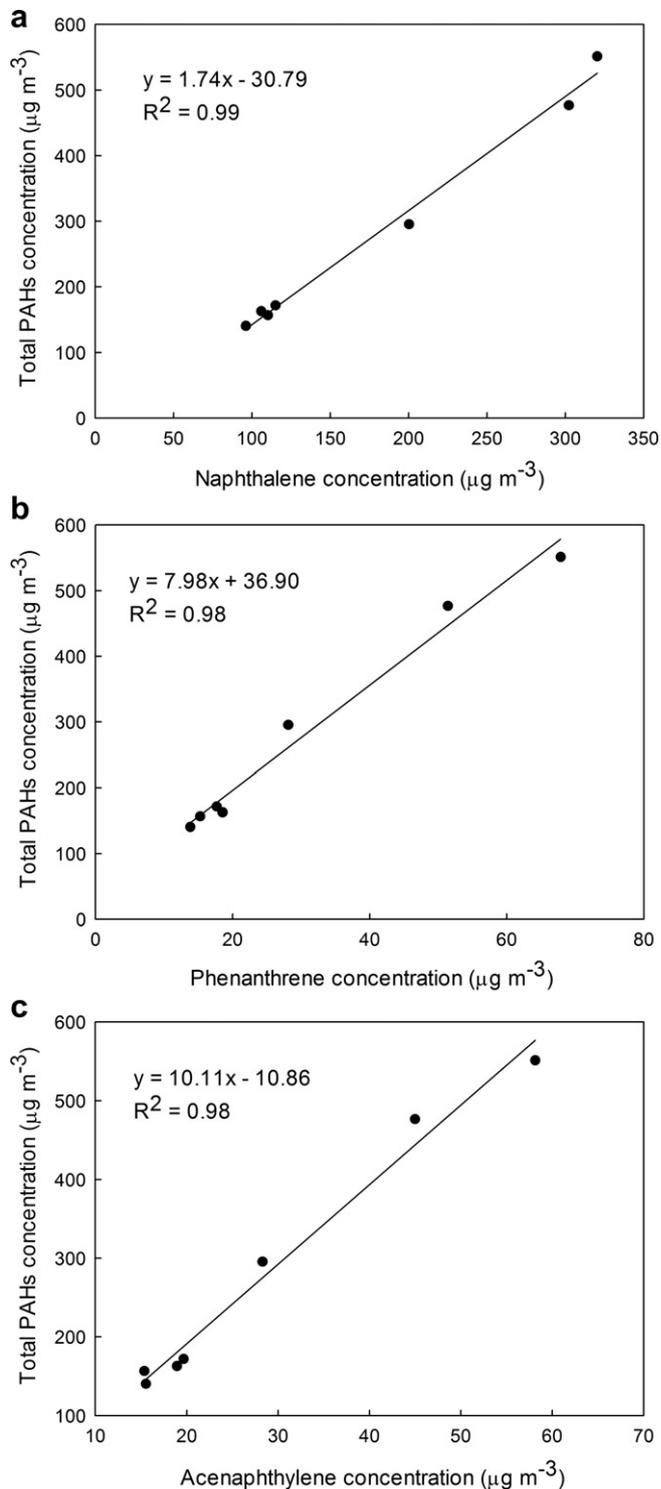

Fig. 2. Individual PAH concentrations vs. total PAH concentration (a) naphthalene (b) phenanthrene (c) acenaphthylene.

Compared to other studies, dry sugarcane EFs are lower than EFs determined for foliar fuels, but agree well with those of crop residue burned in a cookstove. The EFs for whole stalks agree well with those of the foliar fuels for formaldehyde, acetaldehyde and crotonaldehyde compounds. Formaldehyde followed by acetaldehyde and propionaldehyde were the most dominant compounds in all studies.

Yokelson et al. (2008) reported EFs for acetaldehyde and crotonaldehyde from sugarcane burning. It is obvious that the EFs

Table 3
Summary of carbonyl EFs (mg kg^{-1}).

	Sugarcane		Other references
	Dry leaves	Whole stalks	
Formaldehyde	150 ± 33.8	524 ± 316	304.9–1138.1[a], 78.3[b], 135[c], 422[d]
Acetaldehyde	44.8 ± 14.1	323 ± 198	358.0–1146.6[a], 85.1[b], 141[c], 86.3[d], 534[e]
Propionaldehyde	8.3 ± 5.9	51.0 ± 33.6	76.2–207.7[a], 21.6[b], 24.7[d]
Butyraldehyde	ND	3.7	43.0–123.4[a], 12.1[b], 25.6[c]
Benzaldehyde	2.2	9.6 ± 1.8	32.6–72.0[a], 22.2[b], 28.3[c], 12.2[d]
Valeraldehyde	2.5 ± 0.9	2.1 ± 0.5	0.6–175.8[a], 13.1[b], 9.9[c], 1.1[d]
2,5-dimethylbenzaldehyde	ND	33.0 ± 26.2	
Crotonaldehyde	ND	31.1 ± 5.5	39.4–74.9[a], 18.1[b], 32.3[c], 11.2[d], 91[e]

[a] Hays et al., 2002; range of mean EFs for various foliar fuels.
[b] Zhang and Smith, 1999; crop residue in a cookstove.
[c] Zhang and Smith, 1999, wood in a cookstove.
[d] Hedberg et al., 2002; birch wood in wood stove.
[e] Yokelson et al., 2008; sugarcane.

determined for dry sugarcane leaves are much lower than the EF reported by Yokelson et al. (2008). However, the upper range EF of our whole stalk experiments agrees well with that obtained by Yokelson et al. (2008). Yokelson et al. (2008) did not report the condition of sugarcane used (i.e., moisture content), but they reported a MCE of 97.6% (Table 1). They also used a different measurement technique—proton-transfer reaction mass spectrometry (PTR-MS). The differences between the biomass composition, burning conditions, and the measurement technique probably account for the observed differences in the EFs.

3.4. VOCs

VOC EFs are summarized in Table 4. The average precision was 15% based on four sample pairs. Benzene was the most abundant species followed by toluene. The abundance of benzene and toluene as the dominant aromatics is consistent with other biomass combustion studies (Hays et al., 2002).

The VOC EFs obtained in this study were significantly lower than those determined by Hays et al. (2002) for foliar fuels, but are similar with those reported by Jenkins et al. (1996a) for almond and walnut prunings. VOC EFs reported by Yokelson et al. (2008) are significantly higher than those determined in this study and are on par to Hays et al. (2002). As with the PAH and carbonyl EFs, differences in the sugarcane source, burning conditions, and measurement technique may explain the differences in the EFs obtained.

3.5. PM$_{2.5}$

The mean PM$_{2.5}$ EF was 2.49 ± 0.66 g kg^{-1}, based on dry leaf experiments. The EF is in excellent agreement with that determined by Yokelson et al. (2008) (2.17 g kg^{-1}) and is within the range of the current published PM EF (2.3–3.5 g kg^{-1}) for sugarcane pre-harvest burning (USEPA, 1995).

3.6. EC, OC, and tracer species

The average EFs for OC and EC were 0.16 ± 0.09 g kg^{-1} and 0.71 ± 0.22 g kg^{-1}, respectively. The high EC relative to OC ratio found in this study is unique for biomass burning. OC dominates EC in most biomass burning emissions; however, a few exceptions have been reported (McMeeking et al., 2009). Table 5 compares the EC and OC EFs determined in this study to other biomass fuels (which were analyzed by the same method—NIOSH 5040). Sugarcane OC EFs are on the low end of other reported EFs, whereas EC EFs are on the high end.

McMeeking et al. (2009) investigated a wide range of biomass materials and found a negative correlation between the MCE and OC EFs ($r^2 = 0.36$). They found that "leafy" fuels, which had lower MCEs, exhibited the highest OC EFs. EC EFs increased with increasing MCE, particularly for MCE > 93%; however, EC's dependence on MCE ($r^2 = 0.09$) was not as strong as in the case of OC. Instead, EC and other inorganic emissions were found to be a stronger function of the fuel type and composition. Nonetheless, the high EC relative to OC emissions from sugarcane burning can be
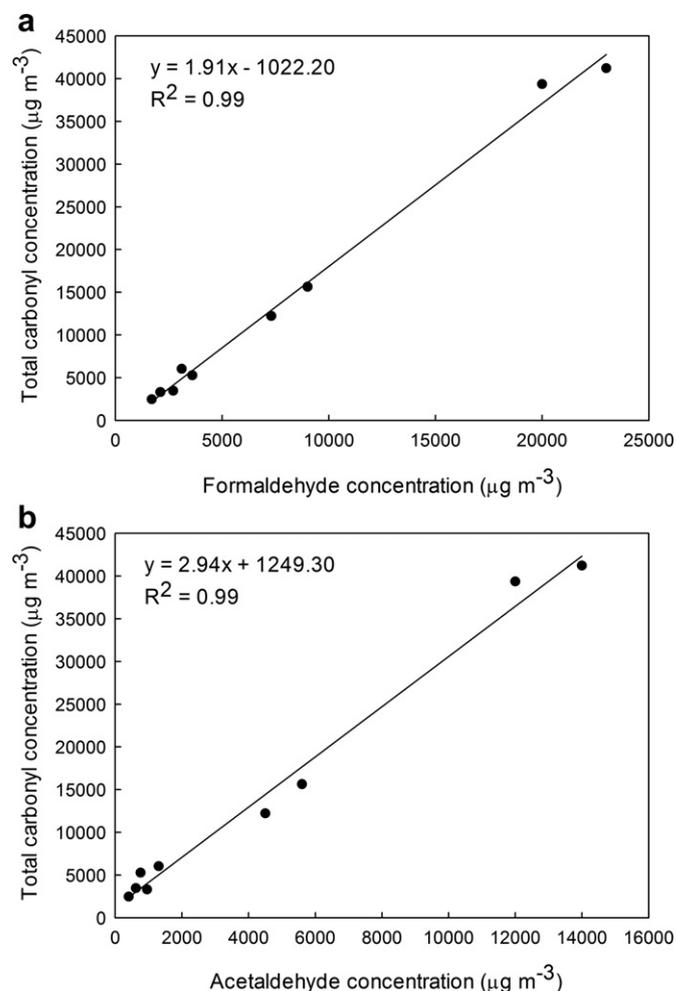

Fig. 3. Individual carbonyl concentrations vs. total carbonyl concentration (a) formaldehyde (b) acetaldehyde.

Table 4
Summary of VOC EFs (mg kg^{-1}).

	Present study	Other references
Benzene	16.5 ± 1.89	16–444[a], 207[b]
Toluene	5.2 ± 0.94	11–351[a], 120[b]
Ethylbenzene	0.81 ± 0.15	60[b]
m,p-Xylenes	0.94 ± 0.45	
Styrene	0.35 ± 0.25	7–652[a]
o-Xylene	0.29 ± 0.19	

[a] Jenkins et al., 1996a; agricultural materials.
[b] Yokelson et al., 2008; sugarcane.

partially attributed to the high MCE observed in this study and may also be a function of the biomass composition. The characteristic EC/OC ratio may be useful in future source apportionment studies to identify and quantify contributions from sugarcane burning.

Table 5 also reports EFs of several anhydrosugar compounds that are common products of the decomposition of cellulose. The EFs observed in this study are within the wide range of EFs reported by other studies, but are expected to be very dependent on the specific burning conditions (Engling et al., 2006). These compounds, particularly levoglucosan (LG) and mannosan (MN), can be used to develop source profiles to be used for source apportionment studies. Specifically, ratios of individual tracer species that are characteristic of certain biomass types can be utilized to provide additional insights into the actual biomass source. For instance, characteristic LG/MN ratios of 3–5 for softwood, 15–25 for hard wood and 40 for rice straw have been reported in previous studies (Engling et al., 2009), while the average LG/MN ratio for sugarcane was 10.

3.7. Emission estimates

In order to understand the magnitude of emissions produced from sugarcane burning, the total yearly emissions of the HAPs investigated in this study were estimated based on the EFs determined in this study. The emission estimates were then compared to the Palm Beach County (PBC) emission inventory from the 2005 national emission inventory and the state of Florida emissions inventory to estimate the relative importance of this practice (USEPA, 2010). To estimate the total emissions, the upper value of the 95% confidence interval for the whole stalk experiments were used when available. For VOC and PM experiments, where whole stalks were not tested, the upper value of the 95% confidence interval for dry leaves was used. EFs were multiplied by the published fuel loading for sugarcane, 7 tons per acre (USEPA, 1995), and

Table 5
Summary of PM$_{2.5}$, EC and OC EFs.

	Sugarcane	Other references[a]
PM$_{2.5}$ (g kg^{-1})	2.49 ± 0.66	3–12.1[b], 3.4–38.3[c], 10.8–28.4[d], 4.71–12.95[e]
OC (g kg^{-1})	0.16 ± 0.09	1.9–6.9[b], 0.5–26[c], 8–27.8[d], 1.23–8.94[e]
EC (g kg^{-1})	0.71 ± 0.22	0.35–0.63[b], 1.4–8.1[c], 0.2–1.3[d], 0.17–0.52[e]
Levoglucosan (mg kg^{-1})	7.87 ± 5.42	150–350[b], 0.14–350[f]
Mannosan (mg kg^{-1})	0.78 ± 0.12	0.011–10.5[f]
Galactosan (mg kg^{-1})	0.72 ± 0.33	0.005–66.5[f]
Xylitol (mg kg^{-1})	0.20 ± 0.14	
Xylose (mg kg^{-1})	0.51 ± 0.10	

[a] EF range is reported when several fuels are reported.
[b] Dhammapala et al., 2007; wheat and Kentucky bluegrass.
[c] McMeeking et al., 2009; various fuels.
[d] Hays et al., 2002; various foliar fuels.
[e] Hays et al., 2005; wheat and rice straw.
[f] Oros et al., 2006; grasses.

Table 6
Contribution of sugarcane burning to emissions inventories.

Compound	Fraction of inventory (%)	
	Palm Beach County	Florida
PAHs		
Naphthalene	1.7	1.3
Acenaphthylene	69	11
Acenaphthene	52	6.2
Fluorene	78	17
Phenanthrene	75	9.5
Anthracene	69	3.6
Fluoranthene	69	3.7
Pyrene	61	2.5
Benz[*a*]anthracene	50	1.0
Chrysene	67	1.5
Benzo[*b*]fluoranthene	77	11
Benzo[*k*]fluoranthene	61	1.4
Benzo[*a*]pyrene	62	2.1
Indeno[1,2,3-*cd*]pyrene	54	0.9
Benzo[*g,h,i*]perylene	23	0.6
Carbonyls		
Formaldehyde	86	16
Acetaldehyde	91	29
Propionaldehyde	89	37
VOCs		
Benzene	3.2	ND[a]
Toluene	0.5	ND[a]
Ethylbenzene	0.4	ND[a]
Styrene	1.6	ND[a]
o,m,p-xylene (mixture)	1.8	ND[a]

[a] Not determined because of insignificance.

an estimate of the sugarcane acreage burned, 335,650 acres, which is based on the 2008 agricultural year.

Table 6 shows the potential contributions of sugarcane burning to the PBC and Florida state inventories for HAPs. Sugarcane field burning did not contribute substantially (<5%) to VOC compound or naphthalene emissions. VOC emissions are dominated by gasoline sources (on-road and non-road equipment) and naphthalene emissions are dominated by industrial boiler fuel combustion in PBC. However, sugarcane field burning plays an important role in the yearly emissions of other PAH (23–78%) compounds and carbonyls compounds (86–91%) in PBC. Additionally, sugarcane burning is estimated to contribute a notable amount at the state level for certain compounds (i.e., acenaphthylene, fluorene, benzo[*b*]fluoranthene, formaldehyde, acetaldehyde, propionaldehyde).

It should be emphasized that field burning is characterized by different burning phases (i.e., smoldering, flaming) and is influenced by a number of variables (meteorological conditions, plant conditions, plant treatment, etc.). EFs are expected to be highly variable during the field burning process as well as during the harvesting period, as the meteorological and plant conditions may change drastically throughout the harvesting season. The EFs reported in this study are most representative of the flaming phase of combustion and may be a conservative estimate of emissions, since previous studies have shown that smoldering combustion exhibits significantly higher emissions of pollutants (Jenkins et al., 1996b).

It should be noted that the ambient concentration levels will depend on many factors such as weather patterns. Ambient air sampling and analysis is, therefore, an important task for providing the necessary data for human health and environmental impact assessment.

4. Conclusions

This study characterized the emissions from the pre-harvest burning of sugarcane fields. EFs were determined for a number of HAPs including PAH, carbonyl and VOC compounds as well as PM$_{2.5}$

in a combustion chamber. Tracer compounds were also investigated and specific compound patterns were identified, which may be helpful for developing source profiles for future apportionment studies.

In general, EFs were consistent between experiments and comparable to other published emission factors for sugarcane burning and other agricultural materials considering the differences in biomass composition, biomass source, and burning conditions. PAH and carbonyl emissions were dominated by low molecular weight compounds, such as naphthalene, formaldehyde and acetaldehyde. The most abundant aromatic VOC compounds measured were benzene and toluene. Additionally, a number of unique compound ratios were observed that may be helpful for source apportionment studies.

Consistent with previous similar studies, our experiments show that EFs are strongly impacted by burning conditions (temperature, intensity, fuel density, combustion efficiency) and biomass properties (moisture content, composition). For example, experiments that used biomass with higher moisture content (i.e., whole stalks) exhibited higher EFs. Also, more intense fires (characterized by higher fuel loading and temperatures) produced lower EFs.

The data from this research will allow the EPA to validate and expand the EFs published in AP-42 for sugarcane pre-harvest burning. The EFs can be used to more accurately calculate the annual emissions from sugarcane pre-harvest burning and to evaluate the contribution of this source to local and state pollutant inventories. Ultimately, with more reliable data, regulatory agencies will be able to more accurately model human and environmental exposure and subsequently, make better management and regulatory decisions.

Acknowledgments

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