

EMISSION FACTORS OF HAZARDOUS AIR POLLUTANTS AND PARTICULATE
MATTER FROM THE PRE-HARVEST BURNING OF FLORIDA SUGARCANE

By

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A THESIS PRESENTED TO THE GRADUATE SCHOOL
OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT
OF THE REQUIREMENTS FOR THE DEGREE OF
MASTER OF ENGINEERING

UNIVERSITY OF FLORIDA

2010

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To my grandparents, Ken Bayless and Constance & Marshall Hall, and my parents, Tim & Jennifer Hall, who have given me courage, inspiration, and freedom to push boundaries and achieve this milestone

ACKNOWLEDGMENTS

First and foremost, I would like to thank my research advisor, Dr. Wu, for his inspiration, hard work and guidance. Dr. Wu's energetic and positive attitude for learning is inspiring to every student. I am thankful for the countless hours he spent helping me write papers and solve research problems, while also giving me the creative freedom to develop my problem solving and thinking skills.

I would also like to thank my committee, Dr. Hsu, Dr. Delfino, and Dr. Ilacqua, for providing me important guidance in my research endeavors. I am especially grateful to Dr. Hsu, my research mentor, for her hard work in developing this research project and for teaching me so many valuable things.

I would like to acknowledge the funding agency for this project—the Palm Beach County Health Department as well as Guenter Engling (Research Center for Environmental Sciences, Academia Sinica, Taipei, Taiwan) for performing the EC/OC analysis.

I am very grateful for my research team, past and present—Jun Wang, Kuei-Min Yu, Nate Topham, Krisha Capeto, Mark Kalivoda, Scott Brown, Lea Ramkellawan, and Heather Waters whom spent countless hours helping me perform experiments, which was always hard work—physically and mentally. I am also thankful for the patience and support my fellow lab mates have shown me.

I would like to thank my parents for their constant love and support, and particularly for all my Dad's technical support building and fixing things for my project. Last, but not least, I would like to thank all my friends who have always been there to help me through stressful times and revive me!

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LIST OF ABBREVIATIONS

CAS	Columbia Analytical Services
CCN	Cloud condensation nuclei
CE	Combustion efficiency
CPM	Condensable particulate matter
DGM	Dry gas meter
DI	Deionized
DLCS	Duplicate laboratory control sample
DNPH	2,3-dinitrophenylhydrazine
EF	Emission factor
EC	Elemental carbon
GC	Gas chromatography
HAP	Hazardous Air Pollutant
HPLC	High performance liquid chromatography
IMPROVE	Interagency monitoring of protected visual environments
FID	Flame ionization detection
LCS	Laboratory control sample
MC	Moisture content
MCE	Modified combustion efficiency
MRL	Minimum report limit
MS	Mass spectrometry
NA	Not applicable
NATA	National air toxics assessment
NIOSH	National Institute for Occupational Safety and Health
OC	Organic carbon

OTM	Other test method
PAH	Polycyclic aromatic hydrocarbon
PBC	Palm Beach County
PCDD	Polychlorinated dibenzo-p-dioxin
PCDF	Polychlorinated dibenzo-p-furan
PM	Particulate matter
QA	Quality assurance
QAPP	Quality assurance project plan
QC	Quality control
Scfm	Standard cubic feet per minute
TEQ	Toxic equivalents
USEPA	United States Environmental Protection Agency
VOC	Volatile organic compound

Abstract of Thesis Presented to the Graduate School
of the University of Florida in Partial Fulfillment of the
Requirements for the Degree of Master of Engineering

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May 2010

Chair: Chang-Yu Wu

Major: Environmental Engineering Sciences

The pre-harvest burning of sugarcane is a common practice used to remove unwanted biomass prior to harvesting. Emission factors (EFs) for sugarcane pre-harvest burning are currently limited and are rated very low (category D) based on their reliability. The objective of this research was to investigate the emission factors of specific polycyclic aromatic hydrocarbons (PAHs), carbonyls, volatile organic compounds (VOCs) and particulate matter (PM_{2.5}) from the pre-harvest burning of sugarcane. Additionally, the elemental carbon (EC) and organic carbon (OC) PM fractions were measured.

An open burning combustion chamber was constructed to simulate field burning. For most experiments, dry sugarcane leaves were burned. A few experiments used whole sugarcane stalks, which exhibited higher moisture contents. The combustion efficiency was monitored to ensure that the combustion chamber accurately represented field burning.

EPA sampling and analysis methods were employed to measure pollutants. PAHs were sampled using quartz filters and PUF/XAD-2 resin cartridges, followed by Soxhlet

extraction and analysis by GC/MS. Carbonyls were collected using DNPH coated cartridges, extracted, and analyzed by HPLC. Gas samples were collected in Tedlar bags for subsequent analysis by GC/MS for VOC compounds. PM_{2.5} was sampled using a size selective cyclone, filter, and impinger train (for condensable particulate matter).

EFs are comparable, but on the low end of EFs published for other types of biomass, which is likely due to the high combustion efficiency observed in this study. The total PAH EF was 7.13 ± 0.94 and 8.18 ± 3.26 mg/kg for dry and whole leaf experiments, respectively. Carbonyl EFs are 201 ± 38.2 and 942 ± 539 mg/kg for dry and whole leaf experiments, respectively. The total VOC EF (for BTEX and styrene compounds) is 23.9 ± 2.62 mg/kg. In all compound classes, the low molecular weight compounds dominated emissions. The PM_{2.5} EF was 2.49 ± 0.66 g/kg, and the OC and EC EFs were 0.23 ± 0.102 and 0.80 ± 0.115 g/kg, respectively.

The results of this project provide the most accurate data available about the EFs of air toxics released during the pre-harvest burning of Florida sugarcane. With more reliable data, the current EFs can be validated and expanded. Subsequently, regulating agencies can more accurately determine human and environmental exposure and therefore make better management and permitting decisions.

CHAPTER 1 INTRODUCTION

Significance of Sugarcane Pre-Harvest Burning

In 2008, 868,000 acres of sugarcane were harvested in the United States. Louisiana and Florida are the largest sugarcane producing states, each harvesting 405,000 and 401,000 acres, respectively in 2008 (National Agricultural Statistics Service, 2009). The remainder of sugarcane is grown in Texas and Hawaii. In Florida, sugarcane agriculture is concentrated in Palm Beach County (PBC) and surrounding areas in the Lake Okeechobee agricultural area.

Prescribed burning of sugarcane fields is practiced to facilitate harvesting by quickly and cheaply removing unwanted biomass (“leaf trash”), 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). Figure 1-1 shows pictures of Florida sugarcane fields being burned. Due to the dry and densely packed nature of the sugarcane, field burning is a quick and intense process—a 40-acre plot will burn in 15 to 20 minutes. In Florida, fields are burned on a plot-by-plot basis (permitted through the Division of Forestry) when climatic conditions are favorable such that smoke plumes will not impact major roadways or densely populated areas. Fields are burned only during the harvest season that, in Florida, extends from October to April.

Emission factors (EFs) quantify the amount of a pollutant released per unit mass burned and are used to develop pollutant emission inventories, which allow regulators to assess contributions from sources on local, regional, and global scales. EFs are also used as inputs for atmospheric dispersion models. Knowing the detailed chemical characterization of emissions can also be useful for source apportionment studies,

which attempt to assign air pollutant emissions to their respective sources based on unique chemical signatures (Dhammapala et al., 2007a; Hays et al., 2002; Liu et al., 2008; Turn et al., 1997; Zheng et al., 2002).

Current EFs for sugarcane pre-harvest burning, published by the United States Environmental Protection Agency (US EPA), are rated “D” on a scale from A to E indicating they are based on a limited data set and thus, are unreliable (US EPA, 1995). The EFs are based on only one study of Hawaiian sugarcane and there is reason to believe other types of sugarcane could differ significantly (Gullet et al., 2006). In addition, only EFs for total particulate matter (PM), CO, and hydrocarbons exist. There are no compound-specific EFs for hazardous air pollutants (HAPs) such as polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs) or carbonyls. According to the 2006 PBC emissions inventory, the practice of sugarcane pre-harvest burning contributes to 17% of VOC emissions, 16% of CO emission and 45% of particulate matter emissions in PBC, highlighting the important contribution of this practice to the local emission inventory of PBC (Palm Beach County Health Department, 2006).

Biomass Burning Emission Factors

Biomass burning encompasses a wide range of combustion activities including: wildfires, prescribed burning, agricultural burning, and biofuel combustion in stoves for cooking and heating. These burning activities have been identified as a significant source of atmospheric emissions that pose significant health risks as well as contribute to local, regional, and global air quality degradation (Jenkins et al., 1996b; Lemieux et al., 2004; Langmann et al., 2009; Turn et al., 1997). Common pollutants released

include: aerosols; gaseous compounds such as VOCs, carbonyls, greenhouse gases; and semi-volatile compounds like PAHs.

Many of the organic compounds (i.e., PAHs, carbonyls and VOCs) that are produced from the pyrolysis of the biomass have known or suspected toxic and carcinogenic effects and are classified as HAPs. Carbonyl and VOC emissions are also of environmental concern because of the important role they play in photochemical smog processes and secondary organic aerosol formation (Hays et al., 2002; Liu et al., 2008; Na and Cocker, 2008; Tsai et al., 2003; Wei et al., 2008; Zhang and Smith, 1999).

Elevated PM concentrations have been linked to increased morbidity and mortality and can contribute to decreased lung function (i.e., coughing, wheezing, asthma attacks), as well as cardiovascular diseases and lung cancer. (Mitra et al., 2002; Pedersen et al., 2005; Russell and Brunekreef, 2009). Particles generated through biomass combustion are often less than 1 μm (aerodynamic diameter), which are particularly harmful to human health since they can travel deep into the respiratory system (Jenkins et al, 1996a). Particles of this size are also of special concern because they contain a major fraction of adsorbed air toxics such as PAHs (Mitra et al., 2002; Pedersen et al., 2005).

PM also has significant atmospheric and environmental impacts, which are largely related to its characteristics (i.e., size and composition). PM from biomass burning is mainly carbonaceous, consisting of elemental carbon (EC) and organic carbon (OC) (Dhammapala et al., 2007a; McMeeking et al., 2009; Na and Cocker, 2008). The fractions of EC and OC are very important in characterizing the impacts of PM, since they have very different effects—EC absorbs solar radiation and has a heating effect,

whereas OC scatters radiation and cools the atmosphere. The relative contribution of EC compared to OC can also be a useful marker for different types of combustion sources (Habib et al., 2008, Zheng et al., 2002)

PM can also affect the hydrological cycle due to its role in cloud formation and microphysical processes. Generally PM acts as cloud condensation nuclei (CCN), which increases cloud cover and rain formation. However, some studies have suggested that the CCN produced from biomass combustion processes, such as sugarcane burning, are so small that they effectively prevent the coalescence of rain, thereby decreasing rainfall (Crutzen and Andreae, 1990; Lara et al., 2005; Twomey and Warner, 1967; Warner, 1968).

Biomass combustion is a complex process characterized by numerous burning phases, which will exhibit a variety of EFs. There are two major burning phases—flaming and smoldering, which can be distinguished by their combustion efficiencies (CEs). Flaming combustion exhibits a high CE, emitting CO₂ as the main product. Smoldering combustion is a lower temperature oxidation process and occurs when there is limited oxygen supply. The smoldering stage exhibits a lower CE and higher emissions of CO and other incomplete combustion products. The contributions from flaming and smoldering in the overall fire event are highly variable and depend on the fire intensity, fuel density, and fuel moisture among other factors. Pollutant emissions are a strong function of the CE, since they form as a result of incomplete combustion (Langmann et al., 2009; Tissari et al., 2008; Ward and Hardy, 1991).

A number of studies have been conducted in order to better estimate the emissions from biomass burning. Generally laboratory studies, which use chambers to

simulate burning, are preferred because of the ease in controlling variables; however, laboratory studies are often criticized for their inability to accurately model field burning conditions. Although laboratory studies may not replicate the complex conditions encountered in the field, they are useful to control variables and replicate burning conditions from experiment to experiment. Laboratory studies also provide information about the entire fire process because the sampled emissions are well mixed over the entire burning process, whereas field samples may be inclined toward flaming or smoldering combustion depending on the sampling location (Chen et al., 2007; Dhammapala et al., 2007b; McMeeking et al., 2009).

Jenkins et al. (1996a) performed a comprehensive study of the EFs of various pollutants from crop and forest residues commonly burned in California. They conducted controlled laboratory simulations in a combustion wind tunnel designed to mimic field conditions. The wind tunnel allowed combustion of a relatively large amount of mass, while also controlling wind speeds—in order to simulate different field conditions (i.e. pile fires vs. spreading fires). CO, CO₂, NO_x, SO₂, hydrocarbons, PM, VOCs and PAHs emissions were measured and EFs were developed. In general, emissions from each fuel source were similar and it was observed that emissions were less dependent on fuel type compared to burning conditions (i.e. wind speed, fuel loading, burning intensity and combustion efficiency). Generally, PAH emissions increased with a lighter fuel loading and increased wind speeds, which led to a weaker flame structure and lower combustion efficiencies. VOC emissions were more variable between the fuel types with emissions from Douglas Fir and Ponderosa Pine being high in comparison to the other fuel types.

Hays et al. (2002) investigated gas-phase and particle emissions from foliar fuels typically burned in U.S. wildfires using a large burn enclosure. The fuels were arranged to mimic field conditions in view of the moisture content (MC), fuel density, and airflow characteristics. $PM_{2.5}$ EFs ranged from 10.8 ± 3.9 g/kg to 33.5 ± 10.5 g/kg and the PM was composed mainly of OC (>80%). The ratio of partitioning between gas-phase to particle-phase PAH emissions ranged from 3:1 to 27:1. Fuels with the highest PAH concentrations in the particulate phase exhibited longer smoldering stages caused by moister and less densely packed fuels—these conditions led to lower CEs and thus higher PAH emissions. Benzene and toluene were the most abundant aromatic hydrocarbons. The 10 hydrocarbons listed as HAPs comprised 18 wt % of the 78 hydrocarbons quantified. Low molecular weight compounds, such as formaldehyde and acetaldehyde, dominated carbonyl emissions and HAP carbonyl compounds comprised 30 wt % of carbonyl emissions.

Hays et al. (2005) investigated the physical and chemical characteristics of PM emissions from wheat and rice agricultural residues in a similar manner as Hays et al. (2002). $PM_{2.5}$ EFs were 4.71 ± 0.04 g/kg and 12.95 ± 0.3 g/kg for wheat and rice fuels, respectively. These EFs are lower than the EFs determined by Hays et al. (2002) for wildfire foliar fuels tested in the same combustion enclosure. The differences were attributed to different burning conditions. Specifically, the foliar fuels were moister than the agricultural materials, and higher MCs may inhibit complete combustion. PM was principally carbonaceous in nature with high OC to EC ratios. Using the EFs for $PM_{2.5}$ obtained in this study, the researchers estimated that wheat stubble burning could account for approximately 15% of anthropogenic $PM_{2.5}$ emissions in Washington and

6% of US emissions. On the other hand, rice stubble burning is estimated to contribute to only 1.5% to the U.S. $PM_{2.5}$ inventory, but may be a major global emission source considering the widespread practice of rice stubble burning around the world.

$PM_{2.5}$ emissions from wheat and Kentucky bluegrass stubble burning were investigated in correlation with the CE by Dhammapala et al. (2006) in a U.S. EPA test burn facility. PM emissions were observed to increase with decreasing CE—PM EFs for wheat stubble were 0.8 ± 0.4 g/kg and 4.7 ± 0.4 g/kg for CEs of 98% and 92%, respectively. Kentucky bluegrass burning exhibited a $PM_{2.5}$ EF of 12.1 ± 1.4 g/kg with an average CE of 90%.

Dhammapala et al. (2007a) measured EFs for PAHs, methoxyphenols, levoglucosan, EC and OC from wheat and Kentucky bluegrass in the same burn facility as Dhammapala et al. (2006). Particulate and gaseous PAH emissions were quantified separately, and emissions were predominantly in the gas phase—81% for wheat emissions and 70% for bluegrass emissions. Lower molecular weight compounds dominated the emissions with acenaphthylene and phenanthrene being the most abundant compounds. The PM mass was dominated by EC and OC—approximately 63% for both wheat and bluegrass. OC emissions were higher than EC emissions, and both the EC and OC emissions decreased with increasing CE.

To investigate the differences in EFs derived from simulated experiments and field experiments, Dhammapala et al. (2007b) conducted field sampling for $PM_{2.5}$, CO, and PAH emissions from Kentucky bluegrass and wheat stubble burning and compared the EFs to their previous laboratory experiments (Dhammapala et al. 2006, Dhammapala et al. 2007a). The researchers found reasonable agreement between EFs derived from

field studies compared to laboratory studies at combustion efficiencies greater than 90%. They concluded that EFs from field and simulated burn experiments will have some differences because of the inherent differences in the situations; however, simulated experiments can provide accurate estimates if the simulated conditions closely mimic the field conditions, for example, the CE.

A large experimental campaign is being conducted at the U.S. Forest Service's Missoula Fire Science Laboratory to characterize smoke emissions from numerous fuels commonly burned in U.S. wildfires as well as a few agricultural fuels, including sugarcane. Physical, chemical, and optical properties of emissions are being studied in order to better understand wildland and prescribed burning effects on visibility impairment and PM inventories. In these studies a comprehensive profile of gaseous and PM emissions has been reported for a variety of fuels (Carrico et al., 2008; Chen et al., 2007; McMeeking, 2009). Yokelson et al. (2008) reported a $PM_{2.5}$ EF for sugarcane as 2.17 g/kg as well as EFs for other VOC compounds. Having a more comprehensive understanding of emission characteristics and influencing factors aids in better predictions of biomass burning on emission inventories, visibility, and radiation budgets.

From previous studies it has been established that pollutant emissions are a strong function of the CE and are influenced by a number of variables. Factors that will have significant impacts on the EFs include meteorology, biomass condition (MC, loading density, pesticide/fertilizer application), burning technique, and fire characteristics (temperature, ventilation, spreading rate, intensity, turbulence) (Dhammapala et al., 2007a; Jenkins et al., 1996a; Lu et al., 2009).

Emission Factors for Sugarcane Burning

The current EFs factors, published in AP-42, for sugarcane burning were developed by E.F. Darley and S.L. Lerman (1975) at the University of California, Riverside. In this study, sugarcane plant material (collected from fields in Hawaii) was combusted in a burning tower. PM (total), CO, hydrocarbon and trace metal emissions were measured. EFs determined by this study are summarized in Table 1-1. The particle size distribution was also measured—92% of particles were below 0.5 μm and less than 2% were greater than 2 μm , demonstrating that most PM is in the fine particle size range.

Meyer et al. (2004) studied the EFs of polychlorinated dibenzo-*p*-dioxins (PCDDs) and furans (PCDFs) from Australian sugarcane using both field and laboratory experiments. The researchers found very different EFs for the laboratory and field experiments—3.7 to 20 pg toxic equivalents (TEQ) per gram of carbon for laboratory experiments compared to 1.2 and 2.9 pg TEQ per gram of carbon in field experiments. They also found differences in the congener and homologue profiles of the PCDD and PCDF compounds between experiment types. PCDFs dominated the emissions in the laboratory experiments, but had much lower contributions in field experiments. The researches linked the discrepancies to the differences in residence time at high temperatures, which is required for dioxin synthesis. In field burning, emissions rapidly rise and are cooled from dilution with ambient air; however, emissions in this laboratory experiment remained at higher temperatures longer, thus further supporting dioxin formation.

Gullett et al. (2006) investigated the EFs of PCDDs and PCDFs from Floridian and Hawaiian sugarcane burning using an open burn combustion facility. The two types of sugarcane exhibited very different EFs. The Hawaiian sugarcane had an average EF of 253 ng TEQ per kg of carbon burned (kg_{Cb}) whereas the Florida sugarcane had EFs of 25 ng TEQ/ kg_{Cb} and 5 ng TEQ/ kg_{Cb} . The researchers speculated that the large difference in EFs was due to the different treatment (fertilizer and pesticide use) and location (affects from sea breezes) of the sugarcane. Chlorine was found to be 13 times higher in Hawaiian cane than in Florida cane, due to the use of KCl by Hawaiian growers and from ocean winds laden with salt. Based on this study, it was estimated that sugarcane burning contributed to 15% of the PCDD and PCDF inventory for the US in 2000, a large contribution of these harmful compounds.

Health and Environmental Impacts from Sugarcane Field Burning

In Brazil, numerous studies have been conducted on the health and environmental impacts of sugarcane burning. Lara et al. (2005) used principal component analysis 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 ($\text{PM}_{2.5}$) mass of PM and 25% of the coarse mode ($\text{PM}_{2.5-10}$) mass of PM. In another study by Kirchhoff et al. (1991), ambient concentrations of CO and ozone (O_3) were observed to be elevated during sugarcane burning periods in Sau Paulo, Brazil. Due to negative environmental and health impacts associated with sugarcane burning, more than 100 sugarcane producers in Sau Paulo, Brazil have agreed to stop the practice of pre-harvest burning by 2017. Instead, fields will be manually harvested and the biomass will be used in cogeneration electric power plants (Reuters, 2007).

Rogge et al. (1997) compared the composition and size distribution of particulate matter from two sites in PBC, Florida where the majority of Florida sugarcane is cultivated. Belle Glade is a rural site dominated by agriculture, particularly sugarcane. Delray Beach is an urban site with numerous industries including electric power production, construction, aircraft testing, computer and electronics manufacturing, waste incineration, and concrete and asphalt production. Belle Glade and Delray Beach showed very similar PM_{10} concentrations from April to September; however, from October to March (during the sugarcane burning season), the average PM_{10} and $PM_{2.5}$ concentrations were 25% and 28.5% higher, respectively, in Belle Glade than Delray Beach. In addition, ambient PAH concentrations in Belle Glade were 20 times higher in January compared to May suggesting the influence of sugarcane pre-harvest burning on the ambient air quality. The ambient PAH concentrations measured in Delray Beach were similar in May and January and were lower than in Belle Glade. This study suggests that the pre-harvest burning of sugarcane could significantly impact the regional air quality of PBC and surrounding areas.

Research Objective

Previous studies demonstrate that sugarcane burning could be a significant contributor to local atmospheric pollution; however, the current EFs for sugarcane pre-harvest burning are limited and unreliable. Further research is warranted in order to better assess the impact of the emissions from this source. 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 simulates field burning. In addition to measuring the mass based $PM_{2.5}$ EF, the composition of PM was

analyzed by measuring the EC and OC fractions. CO and CO₂ concentrations were also measured to evaluate the combustion efficiency.

Table 1-1. Published AP-42 EFs for sugarcane pre-harvest burning (USEPA, 1995)

	Particles (kg/Mg)	CO (kg/Mg)	Methane (kg/Mg)	Nonmethane organic compounds (kg/Mg)
Sugarcane	2.3-3.5	30-41	0.6-2	2-6



Figure 1-1. Florida sugarcane field burning. A) initiation of plot burning by lighting the perimeter of the field. B) picture of smoke plume produced during burning

CHAPTER 2 EXPERIMENTAL METHODOLOGY

Summary of Experimental Approach

Sugarcane biomass was collected from a variety of sources over the course of the study. Both dead (dry) leaves and whole stalks (containing green and dry leaves) were collected for different experiments. Sugarcane was collected from South Florida fields in March 2008, December 2008, and May 2009. Sugarcane was also collected from University of Florida plots in Gainesville, FL (September 2009) and Citra, FL (November 2009 and January 2010). No effort was made to collect sugarcane from a consistent plot of land, but after collection the biomass was handled the same (stored in an outdoor shed in plastic bags). No obvious changes in the dry leaves were observed from the time of collection to burning; however, whole sugarcane stalks gradually dried out during the storage time.

A combustion chamber was built to simulate field burning. Sugarcane was fed into the chamber in a way to create near constant burning conditions. Various pollutants were sampled from the chamber following EPA methods and analyzed to quantify the EFs.

Combustion Chamber Design

An open burning combustion chamber, shown in Figure 2-1, was built to simulate field burning. The combustion chamber consisted of three sections—the combustion section, a cone, and a sample transport duct. The combustion chamber was open to the atmosphere on the bottom to ensure adequate air was available for combustion reactions. The entire chamber and stack was lined with aluminum foil to prevent the

catalytic formation of PAHs, which is associated with steel materials (Jenkins et al., 1996b).

The cone served to direct exhaust gas from the combustion chamber to the stack. To mix the combustion gases before sampling, 2 baffles (made of aluminum) were placed in the stack. Each baffle covered approximately half of the stack area. A draft inducer (Auto-Draft Inucer Model I, Tjernlund Products, Inc.) was employed near the exit of the stack to stabilize the pressure as well as induce excess air into the chamber.

Experimental Procedures

For most experiments, only dry leaf trash was burned. A few experiments burned entire sugarcane stalks, which included the sugarcane stalk, some wet (i.e., green) leaves, and dry leaves. The purpose of the later experiments was to observe the effect of MC and biomass composition on the EFs

To facilitate the burning process, leaves were pre-weighed in batches of approximately 100 g. A butane lighter (BIC) was used to initially light the biomass, after which the sampling was started. Leaves were fed into the chamber at a rate of approximately 100 g every 40 seconds, in order to create near constant burning conditions. The flame was sustained through the constant feeding of biomass during the experiment. Sampling was stopped immediately after the flame was visually observed to cease. In whole stalk experiments, constant burning conditions were attempted, but the combustion was much harder to control due to the more heterogeneous nature of the biomass. After experiments finished, any material (stalks) that did not burn was weighed to determine the net amount of biomass combusted. In dry leaf experiments, post weighing was not performed because the remaining ash was minimal. The sampling and analytical methods were based on EPA promulgated test methods. Some

test methods were adapted for stack sampling applications. Stack sampling meter boxes (containing a pump, dry gas meter (DGM), inclined manometer, and temperature sensors) were used to control the sampling flow rate and record the volume of gas sampled. The meter boxes and dry gas meters were calibrated using a certified dry gas meter once.

Sampling was conducted from a roof positioned near the sampling point; therefore, sampling lines were kept less than 12 inches, minimizing losses in the sampling lines. Additionally, all sample lines were heated to prevent condensation within the sampling lines. Only one pollutant was sampled per experiment. The sampling time and flow rates varied between each method and are discussed in more detail in the following sections. The sampling point was approximately 8 duct diameters downstream of the baffles, to be consistent with EPA stack sampling protocols (USEPA, 2000a). Due to the short duration of experiments and limitations in space, the sampling probe was kept at the same point throughout the experiment. To test whether sampling at a single point was representative of the entire stack cross-section, a gas uniformity test was conducted.

For each sample, a field data sheet was completed including the following information: experiment date, time, name; ambient temperature and pressure; sampling rate; mass of leaves burned; DGM start and finish volumes; DGM inlet and outlet temperatures; DGM pressure; and any comments about the experiment. Prior to the start of experiments, leak checks were performed by closing off the sampling inlet and observing movement on the DGM dial. If a leak was detected, the sampling line was

inspected and leaks were repaired. If the leak could not be repaired, the leak rate was recorded and the sample volume was corrected.

PAH, carbonyl, and VOC sample extraction and analysis was performed by Columbia Analytical Services (CAS), which is certified by the Florida Department of Health (NELAP Certification E871020).

A formal Quality Assurance Project Plan (QAPP) was prepared and approved by the EPA to ensure meaningful data was obtained. When procedures were changed, the QAPP was updated and submitted for review and approval. Quality assurance (QA) and quality control (QC) measures are described in the following sections.

Uniformity Test

Since samples were collected from one point in the stack, it is important to evaluate whether the exhaust gases were uniformly mixed at the point of sampling. To accomplish this, oxygen concentrations were measured with a real-time oxygen monitor (Rapidox 3000) at five random points in the stack cross-section. 100 g of sugarcane was burned, and the oxygen concentrations were measured every second during the burning cycle, which lasted approximately 2 minutes. A one-way ANOVA statistical test was performed to identify any significant concentration differences between various points in the duct cross-section.

Polycyclic Aromatic Hydrocarbons

PAH sampling and analysis was based on EPA method TO-13A (USEPA, 1999a), modified for stack sampling. The PAH compounds investigated include: naphthalene, acenaphthylene, acenaphthene, fluorene, phenanthrene, anthracene, fluoranthene, pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene,

benzo[a]pyrene, indeno[1,2,3-*cd*]pyrene, dibenz[a,h]anthracene, and benzo[g,h,i]perylene. The PAH compound structures are displayed in Figure 2-2.

Sampling

The PAH sampling train is shown in Figure 2-3. PAH sampling was performed by passing sample gas through a quartz filter (to collect particulate PAHs) and a sorbent cartridge containing polyurethane foam (PUF) and XAD-2 resin (to collect semi-volatile PAH compounds). All samples lines were composed of stainless steel and heated with heating tape during sampling. Because PAH compounds exist partially in the particulate phase, sampling was performed isokinetically. The sampling flowrate was manipulated in order to match the sampling velocity through the nozzle to the measured stack velocity.

Prior to sampling, the quartz filters were baked at 400 °C for 5 hours and stored in a dessicator until use. Sorbent cartridges were prepared, cleaned, and certified clean by CAS. In between experiments, samples lines were rinsed with hexane and air-dried.

Following sampling, filters and sorbent cartridges were immediately wrapped in hexane rinsed aluminum foil and stored below 4°C until shipment. Samples were usually shipped the next day, except in the cases where experiments were conducted on Friday or Saturday. Samples were shipped in dry ice for preservation and were extracted within 7 days of collection.

Analysis

CAS performed all sample extraction and analysis procedures in accordance with EPA Method TO-13A. Briefly, filters and cartridges were Soxhlet extracted together in a mixture of 10% diethyl ether in hexane for 18 hours and the extract was concentrated

using a turbo-vap evaporator (Zymark). The extract was then injected into a gas chromatograph (GC) (Hewlett Packard 58900II+) with a fused silica capillary column to separate the analytes and a mass spectrometer (MS) (Hewlett Packard 5972A) was used in the full range data acquisition (SCAN) mode to detect the analytes. Compounds were identified by comparing the mass spectra of the samples to those of reference materials. The compound concentrations were quantified using an internal standard calibration, whereby the analyte's responses were compared to the responses of internal standards that were added to the sample prior to the analysis.

QA/QC

A number of QA/QC measures and samples were taken in order to ensure the integrity of the PAH data:

- One field blank was collected to detect any contamination introduced through handling or storage procedures. The field blank was treated the same as test samples; however, no sample air was drawn through the cartridge.
- Ambient blank samples were collected at the beginning of each experiment day to measure the background concentrations of the compounds of interest in the area.
- Two samples, collected in parallel, were used to measure the precision of the sampling and analysis. Parallel samples were collected in 40% of experiments.
- A laboratory method blank was run with each batch of samples analyzed to ensure there was no contamination in the laboratory methods or in the cartridge itself. The laboratory method blank was a clean sorbent cartridge and filter that was treated the same as a sample. All analytical steps were conducted the same as sample analysis—using all reagents, standards, surrogate compounds and glassware that were used for the sample analysis.
- Laboratory control sample (LCS) and a duplicate laboratory control sample (DLCS) were run with each batch of samples analyzed. LCSs and DLCSs served to monitor the extraction efficiency of target analytes from clean sorbent cartridges. Clean sorbent cartridges were spiked with known concentrations of the target analytes and processed with the same extraction and analysis procedures as the field samples. LCSs and DLCSs were run with every group of samples analyzed.

- Surrogate compounds (fluorene-d10 and pyrene-d10), which are similar to the target compounds but are not naturally found in environmental samples were spiked onto the method blank, lab control sample, duplicate lab control sample, and each sample analyzed to evaluate and monitor for unusual matrix effects, sample preparation errors, and analysis errors.

Carbonyls

Carbonyl sampling and analysis followed a modified EPA Method TO-11A (USEPA, 1999b), adapted for stack sampling. Carbonyl compounds that were investigated include: formaldehyde, acetaldehyde, propionaldehyde, crotonaldehyde (total), butyraldehyde, benzaldehyde, isovaleraldehyde, valeraldehyde, o-tolualdehyde, m,p-tolualdehyde, n-hexaldehyde, and 2,5-dimethylbenzaldehyde.

Sampling

The carbonyl sampling train is shown in Figure 2-4. Commercially available cartridges pre-coated with 2,4-dinitrophenylhydrazine (DNPH) (Supleco) were used to sample carbonyls. A LpDNPH (Supleco) ozone scrubber was placed before the DNPH cartridge to remove ozone interferences. The sampling line was made of stainless steel and brass and was heated with heating tape. Between experiments the sample line was purged with pure nitrogen gas.

Following sampling, cartridges were stored in a freezer until shipping. Cartridges were sent to CAS (with dry ice for preservation) and were analyzed within 5 days of collection.

Analysis

CAS performed all sample extraction and analytical procedures in accordance with Method TO-11A. The sample cartridges were eluted with acetonitrile and analyzed by isocratic reverse phase high performance liquid chromatography (HPLC) (Waters LC

Module I Plus or Hewlett Packard HP 1050) with an ultraviolet absorption detector operated at 360 nm.

QA/QC

A number of QA/QC measures and samples were taken in order to ensure the integrity of the carbonyl data:

- One field blank was collected to detect any contamination introduced through handling or storage procedures for each lot of DNPH cartridges used. The field blank was treated the same as test samples; however, no sample air was drawn through the cartridge.
- Ambient blank samples were collected at the beginning of each experiment day to measure the background concentrations of the compounds of interest in the area.
- A breakthrough test was conducted by placing two DNPH cartridges in series. The backup cartridge was analyzed to ensure no compounds were detected (i.e., no breakthrough occurred during sampling).
- Parallel samples were collected in 4 out of 5 experiments to determine the precision.
- A blank cartridge was analyzed with each batch of samples to detect contamination from the sample cartridges or analytical methods.

Volatile Organic Compounds

EPA Method 18 was applied for the sampling of VOCs (USEPA, 2000b) and EPA Method-TO-15 (USEPA, 1999c) was applied for the analysis (performed by CAS). Benzene, toluene, *o,m,p*-xylenes, ethylbenzene and styrene compounds were investigated.

Sampling

Method 18 involves collecting gas samples in Tedlar bags using a Vac-U-Chamber (SKC). The Vac-U-Chamber is a rigid air sample box that allows for bags to be filled directly by using negative pressure. The sample bag (contained in the Vac-U-Chamber) was connected to the sample probe with Teflon tubing. The air-tight chamber was

evacuated with a vacuum pump causing the Tedlar bag to fill with sample gas. Figure 2-5 shows a picture of the Tedlar bag contained within the Vau-U-Chamber prior to the start of an experiment

Prior to use, Tedlar bags were purged 5 times with pure nitrogen gas. Tedlar bags were never reused. After samples were collected they were protected from UV light until analysis. The time between sample collection and analysis was minimized as much as possible and never exceeded 72 hours.

Analysis

CAS performed the analysis in accordance with Method TO-15. The analysis procedure involves pre-concentrating a known volume of air on a solid adsorbent trap and then analyzing with GC/MS (Agilent 6890N/5975). Analytes were identified by comparing the mass spectra of the samples to those of reference materials. The compound concentrations were quantified using an internal standard calibration, whereby the analyte's responses were compared to the responses of internal standards that were added to the sample prior to the analysis.

QA/QC

A number of QA/QC measures and samples were taken in order to ensure the integrity of the data:

- Ambient blank samples were collected at the beginning of each experiment day to measure the background concentrations of the compounds of interest in the area.
- Parallel samples were collected in 100% of the VOC experiments performed.
- Method blanks were performed to detect contamination in the analytical procedures.
- With each batch of samples analyzed, a 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.

- Surrogate compounds (1,2-dichloroethane-d4 and toluene-d8) were spiked into each sample analyzed to measure their recovery.
- To determine EPA Method 18's ability to accurately measure all compound concentrations, a canister with spiked compounds in known concentrations was sampled exactly how experiments were conducted. The bag sample was then analyzed, and the recovery of each compound was determined.

PM_{2.5}

PM_{2.5} sampling was based on EPA's Other Test Methods (OTMs) 27 and 28 (USEPA, 2008a; USEPA, 2008b) to measure the filterable and condensable PM (CPM), respectively. Filterable PM is defined as any PM that can be collected on the filter at the sampling point temperature. CPM is any PM that may form or condense as the exhaust gases are cooled to below 85 °F. Since the stack gas temperature in our experiment exceeded 85°F, an impinger train (based on OTM 28) was used to cool the exhaust gases and collect the CPM in some experiments. In addition to determining the PM_{2.5} mass EF, PM samples were also collected on tissuquartz filters to determine the mass emission rates of EC and OC.

Sampling

Figure 2-6 displays the sampling train, which was modified slightly from Methods 27 and 28. 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 was added to collect and analyze CPM. The impinger train serves to cool the gas to <85 °F. A temperature sensor was used in the impinger train to ensure the temperature was less than 85 °F at the CPM filter. CPM was collected in the impinger

train and on a Teflon filter (Zefluor, Pall Life Sciences). PM samples for the EC/OC analysis were collected the same as filterable PM samples except a tisuquartz filter (Catalog number 2500QAT-UP, Pall Life Sciences) was used in place of the glass fiber filter.

The actual cut size of the cyclone is dependent on the gas viscosity, which is a function of temperature. Since the average temperature for each experiment varied, the actual cyclone cut-points varied slightly, but can be calculated using Equation 2-1, which was determined in the cyclone calibration performed by the manufacturer.

$$D_{50} = (0.024\mu - 3.09)Q^{-0.80} \quad (2-1)$$

where D_{50} is the cyclone cut-point (μm), Q is the sampling flow rate (acfm) at the inlet of the cyclone at actual stack temperature and pressure, and μ is the gas viscosity (micro-poise) that is calculated using Equation 2-2 .

$$\mu = 174.4 + 0.406T \quad (2-2)$$

where T is the stack gas temperature in $^{\circ}\text{C}$.

Glass fiber and Teflon filters were baked for at least 3 hours at 105°C prior to use. Tisuquartz filters used for EC/OC analysis were baked at 550°C for 12 hours and allowed to cool for 12 hours to remove any residual carbon in the filters. All filters were wrapped in aluminum foil and stored in a dessicator chamber until use.

Analysis

Following sampling, the glass fiber filters were placed in a Petri dish and into a dessicator chamber to equilibrate at low humidity for at least 24 hours before determining the post weight. 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. A microbalance (Model MC 210 S, Sartorius Corp.; readability – 10 µg) was used for all weighing. Filter and dishes were weighed 3 times to determine the average mass and were repeatedly weighed at intervals of at least 6 hours to ensure the weight was constant (defined as having a weight change of less than 0.5 mg over at least a 6 hour period).

For the CPM recovery, the impingers were rinsed three times with ultra-high purity deionized (DI) water to collect inorganic soluble PM. Following the water rinses, the impingers were rinsed once with acetone and twice with methylene chloride to collect the organic fraction of the PM. The inorganic (i.e., water) and organic (i.e., acetone and methylene chloride) rinses were kept separately. The CPM filter was extracted in an ultrasonic bath three times with DI water and three times with methylene chloride and the extracts were added to the inorganic and organic rinses, respectively. In accordance with Method 28, the water rinses were extracted with methylene chloride in a separatory funnel to remove any organic PM that may have been included with the initial water rinses. The inorganic fraction was taken to dryness, 100 mL of DI water was added to re-dissolve the residual, and the mixture was titrated to a pH of 7.0 using 0.1 N ammonium hydroxide to neutralize acids and remove waters of hydration. Then both the inorganic and organic rinses were allowed to evaporate to dryness and the remaining residue was weighed to determine the condensable PM mass.

The glassware used in the sampling train and analytical procedures was meticulously cleaned before use. Glassware was soaked in a soapy water bath, cleaned in an ultrasonic bath with DI water for at least two, sixty minute cycles, and rinsed with acetone and two rinses of methylene chloride. Finally, the glassware was

baked at 300 °C for 6 hours. During storage and transportation to and from the field, all glassware openings were covered using aluminum foil.

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). In the analysis, a portion of the filter is heated at distinct intervals to 600 °C in a pure helium atmosphere to volatilize the organic carbon. The sample is then cooled and re-heated at intervals in a 2% oxygen in helium atmosphere to evolve the elemental carbon. The evolved fractions are oxidized to CO₂ and reduced to CH₄ and analyzed by a flame ionization detector (FID).

QA/QC

A number of QA/QC measures and samples were taken in order to ensure the integrity of the PM data:

- Ambient blanks were collected in the field at the beginning of each experiment day for filterable particulate matter and EC/OC filter samples. Because the temperature was always below 85°F in the field for ambient samples, the impinger train was not used as part of these blank experiments.
- Lab blanks were run using the entire CPM impinger train setup and reagents used for analysis. The lab blank served to measure the contamination introduced into the analysis from the rinsing reagents and sealant used to lubricate the impinger connections.
- Filter laboratory blanks were used in the EC/OC analysis. The laboratory filter blank served to detect any background carbon concentrations within the clean filter.

Flue Gases

To evaluate the combustion conditions of our experimental system, CO, CO₂ and O₂ concentrations were measured in a few experiments. Gas monitors were rented for

one 1 month; therefore, flue gases were not monitored during every sampling campaign. However, since burning procedures were consistent across all experiments the combustion efficiency is expected to be similar.

Table 2-1 summarizes the instruments used for the gas monitoring. Gases were sampled from one sample probe in the stack and passed through a gas conditioner (Universal Dual Pass) to cool and dry the exhaust gases before directing them to the gas analyzers. Data was recorded on a 1 second, real-time basis and recorded on a datalogger (Monarch 2000).

CE is defined as the fraction of carbon released as CO₂. In this study, the modified combustion efficiency (MCE) was determined using Equation 2-3, which assumes all of the carbon is released as CO or CO₂.

$$MCE = \frac{\Delta[CO_2]}{\Delta[CO_2] + \Delta[CO]} \quad (2-3)$$

$\Delta[CO]$ and $\Delta[CO_2]$ are the mass concentrations of CO and CO₂ in excess of the background. Previous studies have demonstrated that over 95% of carbon is released as CO or CO₂; therefore, it is accurate to estimate the CE without measuring hydrocarbons or particulate matter (Ward and Hardy, 1991; Gupta et al., 2001; Chen et al, 2007).

Instruments were calibrated before each experiment using EPA protocol gases. The CO analyzer was zeroed with zero air and calibrated at 2173 ppm. The CO₂ monitor was zeroed with high purity nitrogen and calibrated at 6% CO₂. The oxygen monitor was zeroed with pure nitrogen and calibrated with ambient air (20.9% O₂). Span checks were performed on the CO and CO₂ monitors using 1088 ppm CO and 3% CO₂

gas. Span checks served to ensure the linearity of the instrument response and calibration.

Temperature and Pressure

In order to calculate the velocity in the stack and the chamber volumetric flowrate, the pressure and temperature were monitored in the stack in accordance with EPA Method 2 (USEPA, 2000c). The pressure was measured using a s-type pitot tube connected to an inclined manometer and the temperature was measured with a thermocouple. Pressure and temperature were monitored throughout the experiment at centroid points along a horizontal traverse of the stack at the same level as the sampling point. Figure 2-7 shows the pressure and temperature measurement points.

For longer sampling periods, the pitot tube and thermocouple were moved along the traverse to each measurement point; however, for shorter sampling periods they were kept stationary at one point. The pressure and temperature were recorded at regular intervals (about every 30 sec.). Using the average temperature and pressure measured, the average stack velocity was calculated using Equation 2-4.

$$v_s = K_p C_p \sqrt{\Delta P_{avg}} \sqrt{\frac{T_{s(avg)}}{P_s M_s}} \quad (2-4)$$

where v_s is the average stack gas velocity (ft/s), K_p is a constant equal to 85.48 ft/s (lb/lb. mole - R)^{1/2}, C_p is the pitot tube coefficient (0.84), $T_{s(avg)}$ is the average stack temperature (R), P_s is the absolute stack gas pressure (in. Hg) (assumed to be atmospheric pressure since the sampling point was near the exit of the stack, which was at atmospheric pressure), and M_s is the molecular weight of the stack gas (calculated from flue gas data to be 29.2 g/mole).

The standard volumetric flowrate was calculated using Equation 2-5.

$$Q = 60(1 - B_{ws})v_x A \left[\frac{T_{std} P_s}{T_s P_{std}} \right] \quad (2-5)$$

where Q is the volumetric flow rate (scfm), B_{wo} is the proportion of volume of water vapor in the gas stream, A is the cross-sectional area of the stack (ft²), T_{std} is the standard condition temperature (530 R), and P_{std} is the standard pressure (29.92 in. Hg). The B_{wo} of the gas stream was calculated by measuring the weight change of an impinger filled with silica gel submerged in an ice bucket (to condense the water). Since B_{wo} was found to be less than 0.01, it was neglected when calculating the volumetric flowrate.

EF Calculation

EFs were calculated using Equation 2-6 (Dhammapala et al., 2006), which assumes the chamber to be well mixed.

$$EF = \frac{\Delta C_x \times Q_{chamber} \times t}{m_{burned}} \quad (2-6)$$

where ΔC_x is the measured pollutant concentration minus the ambient concentration, $Q_{chamber}$ is the flowrate through the chamber, t is the sampling time, and m_{burned} is the mass of biomass burned. In the case 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 (530 R and 29.92 in. Hg).

Table 2-1. Gas analyzer summary

Gas	Analyzer model (manufacturer)
O ₂	Rapidox 3000 (Cabridge Sensotec)
CO	48C (Thermo Electron Corporation)
CO ₂	1400 (Servomex)

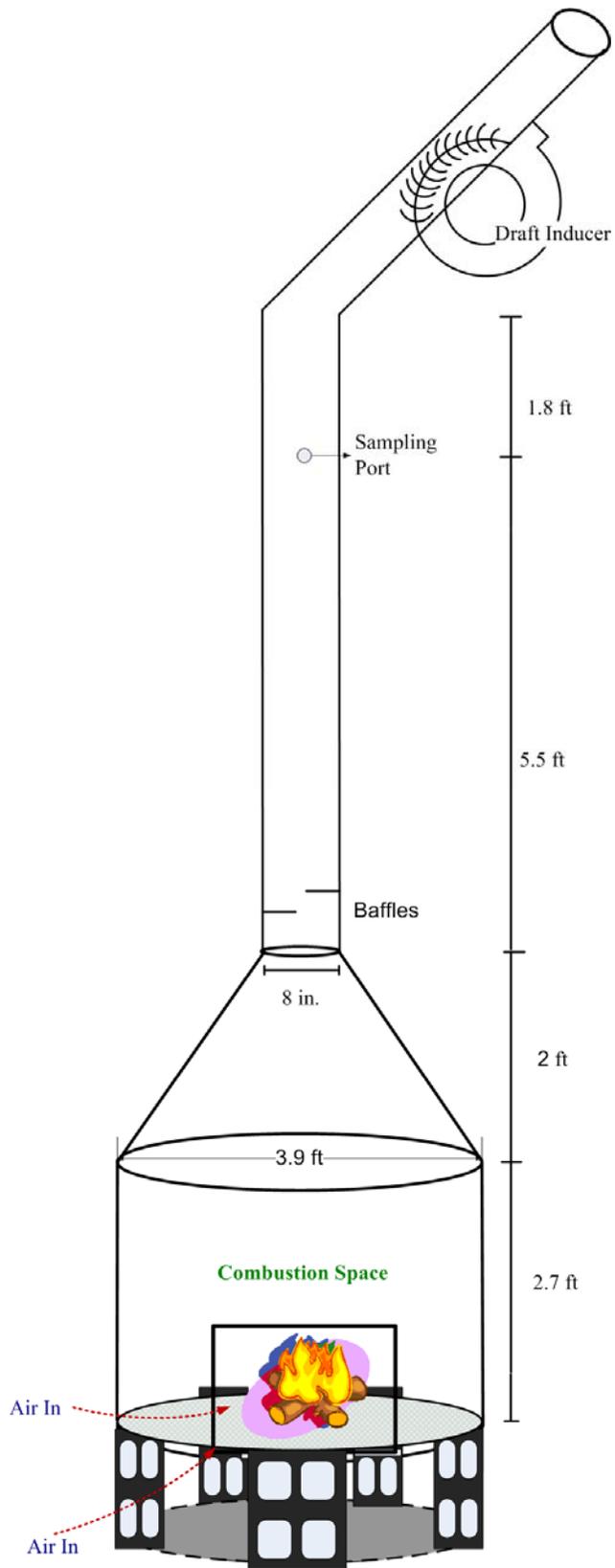
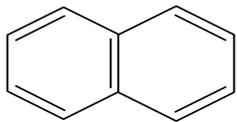
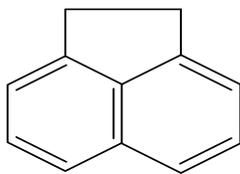


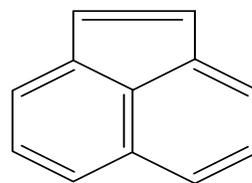
Figure 2-1. Combustion chamber



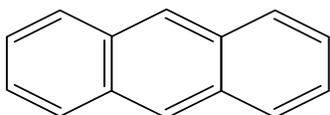
Naphthalene



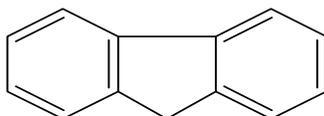
Acenaphthene



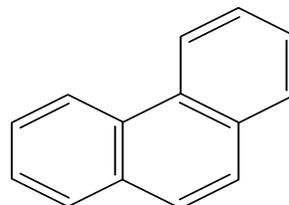
Acenaphthylene



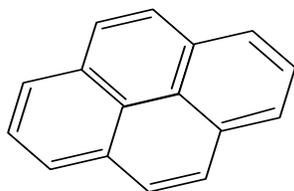
Anthracene



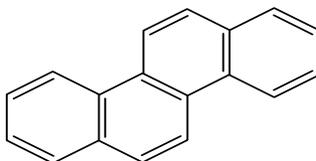
Fluorene



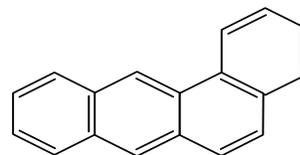
Phenanthrene



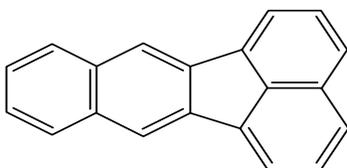
Pyrene



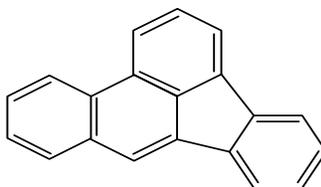
Chrysene



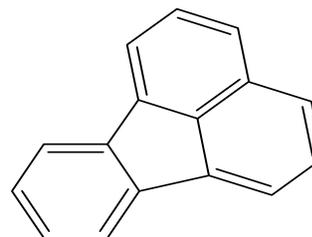
Benz[a]anthracene



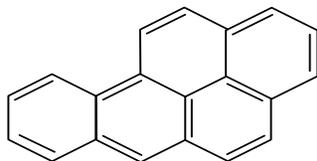
Benzo[k]fluoranthene



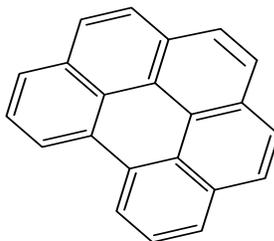
Benzo[b]fluoranthene



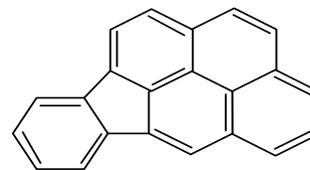
Fluoranthene



Benzo[a]pyrene



Benzo[g,h,i]perylene



Indeno[1,2,3-c,d]pyrene

Figure 2-2. PAH compound structures

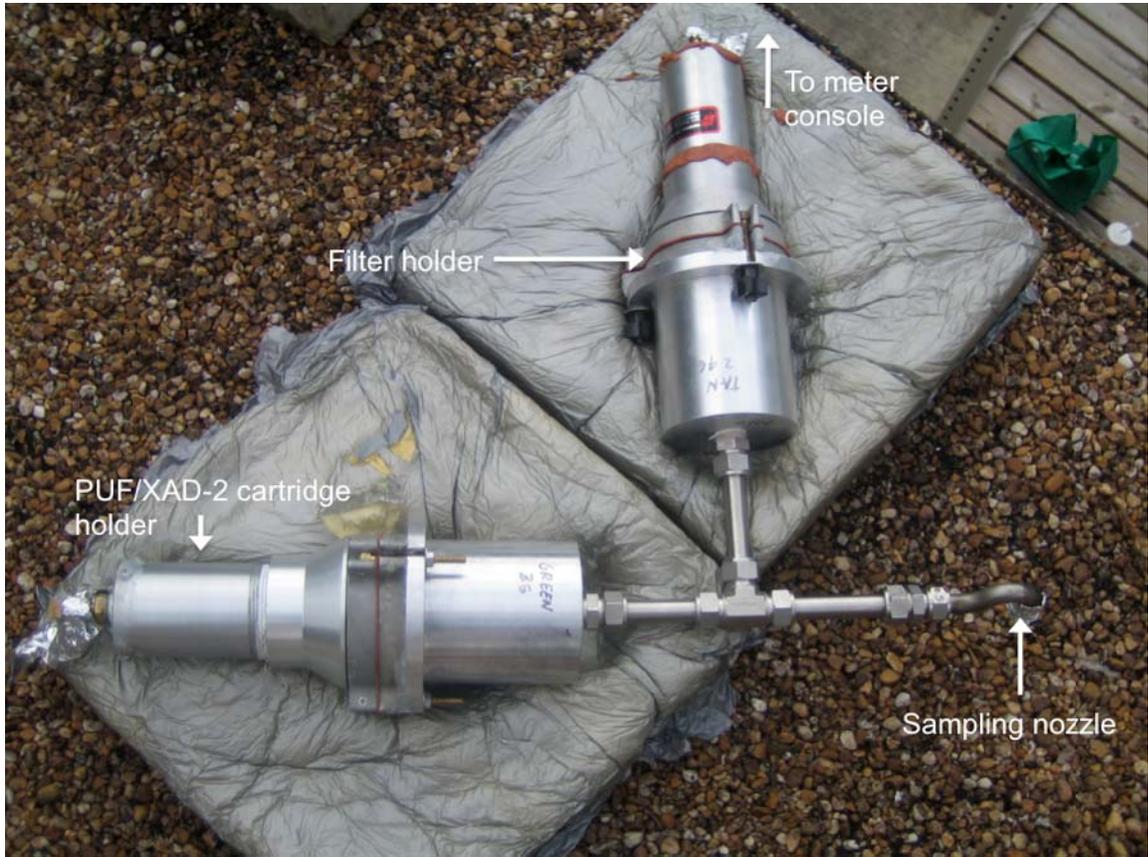


Figure 2-3. PAH sampling train

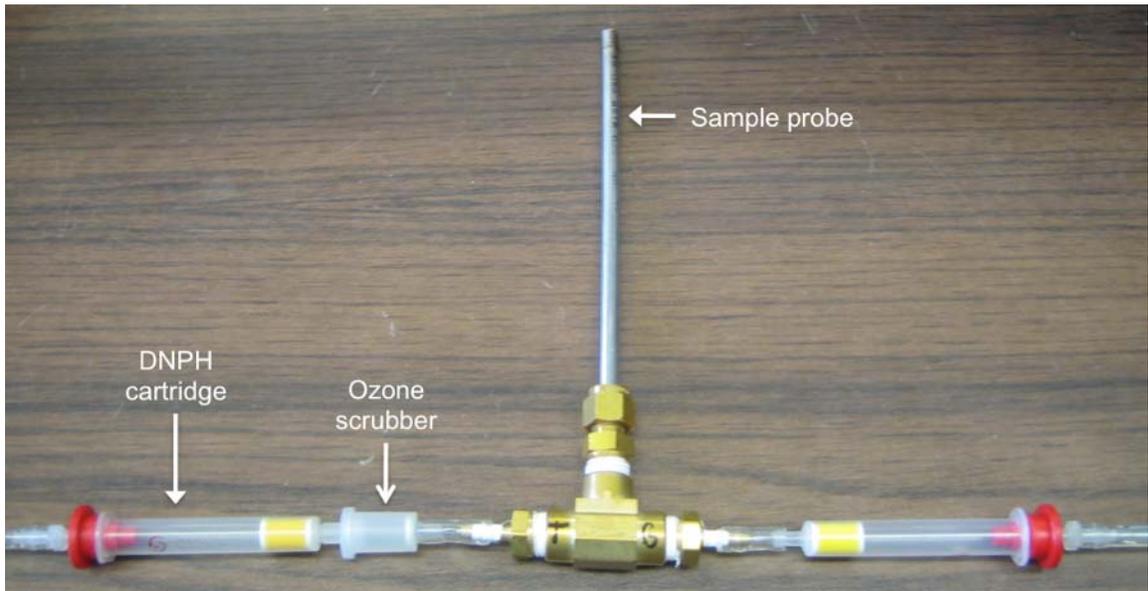


Figure 2-4. Carbonyl sampling train



Figure 2-5. Tedlar bag contained in Vac-U-Chamber

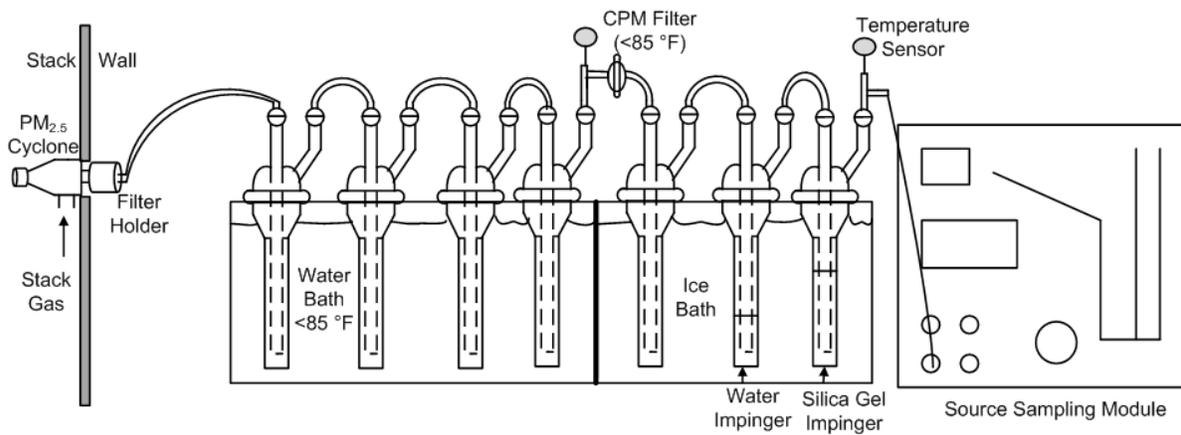


Figure 2-6. PM_{2.5} sampling train

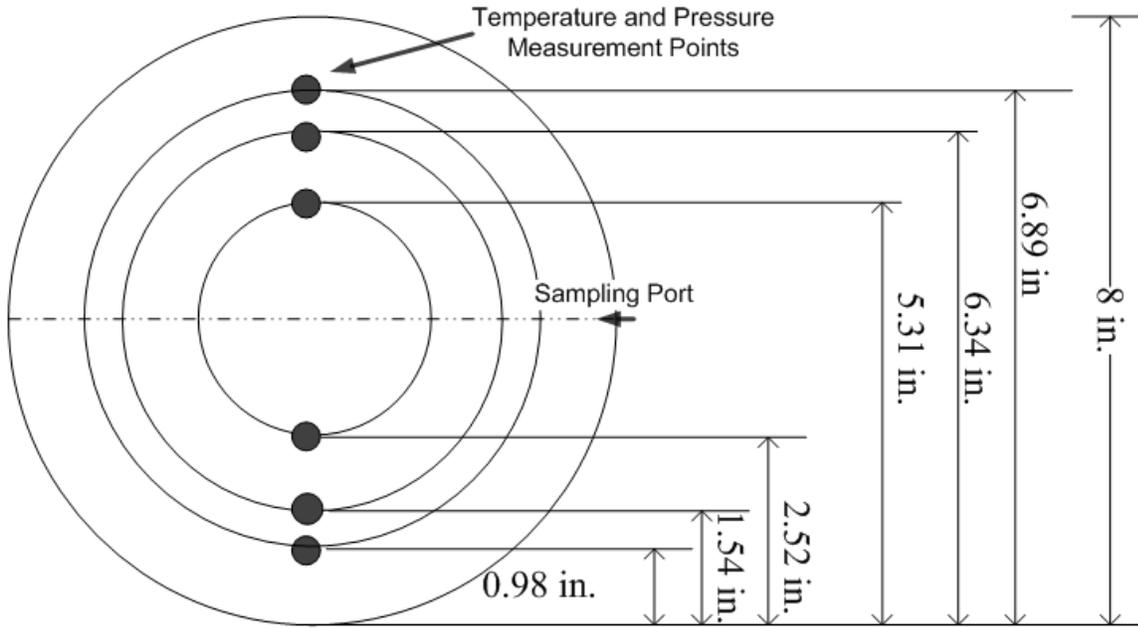


Figure 2-7. Pressure and temperature measurement points

CHAPTER 3 RESULTS

Uniformity Test

Figure 3-1 shows the O₂ gas concentrations at each measurement point over the duration of the test. To identify any significant concentration differences between the measurement points, a one-way ANOVA statistical analysis test was performed. A p value of 0.33 was obtained, signifying there were no significant differences among the measurement points (i.e., the combustion gases are uniformly mixed). Therefore, sampling at one point in the stack cross section provided a representative measurement.

Flue Gases

Flue gases were recorded during 3 major burning events for dry leaves. Figure 3-2 shows an example plot of the flue gas concentrations and MCE for a burn of 2 kg of dry leaves. The leaves were added at a rate of 100 g about every 40 seconds. The peaks and valleys in the flue gas concentrations correspond to the changing intensity of the fire as a result of the feeding process. The dashed line marks the time when the flame was visually observed to cease (at which pollutant sampling was stopped). At this point the MCE drops due to the high CO relative to CO₂ concentrations associated with the smoldering phase of combustion.

Based on the three experiments, the average MCE was 98.5 ± 0.21 for the flaming phase of combustion. The high combustion efficiencies exhibited in this experiment indicate PAHs the dominance of flaming combustion in this studied scenario.

PAHs

Five PAH experiments were conducted, totaling 7 samples (two experiments collected parallel samples). Tests 1-3 used solely dry leaves, whereas Tests 4 and 5 used whole sugarcane stalks with a mixture of dry and green leaves. Table 3-1 summarizes the sampling conditions for each experiment. Samples were named for their sample type (i.e. ambient, field blank or test), the number denotes the experiment number, and the letter (i.e. a and b) denotes parallel samples. Sampling conditions are not applicable (NA) for the field blank, since no sample was taken for this test.

Due to the complex nature of the extraction and analytical procedures in Method TO-13A, some analytical bias is expected. Hence, extensive QC samples (surrogate spikes, LCS, and DLCSs) are used to monitor for these effects. To account for the differences in extraction and recovery efficiencies between experiments, concentrations were adjusted based on the compound recoveries in the LCS and DLCS samples as well as the surrogate compound recoveries. Equation 3-1 shows how the adjusted (“true”) concentration was calculated.

$$Concentration_{true} = \frac{Concentration_{measured, sample} \times \% recovery_{surrogate, LCS \& DLCS}}{\% recovery_{compound, LCS \& DLCS} \times \% recovery_{surrogates, sample}} \quad (3-1)$$

where $Concentration_{measured, sample}$ is the measured concentration in the sample, $\%recovery_{surrogates, LCS \& DLCS}$ is the average % recovery of the surrogate compounds in the LCS and DLCS, $\%recovery_{compound, LCS \& DLCS}$ is the average % recovery of the specific PAH compound in the LCS and DLCS, and $\%recovery_{surrogates, sample}$ is the average % recovery of the surrogate compounds in the sample. Each experiment and the results are explained in detail in the following sections.

Test 1 (5/14/09)

Table 3-2 summarizes the sample concentrations, minimum reporting limit (MRL), and EFs for Test 1. The total EF for this experiment was 5.92 mg/kg—dominated by naphthalene, which contributed to 68% of PAH emissions. The other major compounds were acenaphthylene and phenanthrene, which contributed to 11% and 10%, respectively, to the total PAH EF. Heavier molecular weight compounds were not detected (ND) in this test. Table 3-3 summarizes the QA/QC results for the LCS and DLCSs as well as surrogate compound recoveries. The sample concentrations and EFs presented in Table 3-2 have already been corrected to account for the recovery efficiencies.

Test 2 (5/27/09)

Two samples were collected in parallel in Test 2. Table 3-4 summarizes the results of Test 2 and Table 3-5 summarizes the QA/QC results. The total PAH EF was 7.21 ± 0.27 mg/kg. Again, the most abundant compound was naphthalene comprising 66% of PAH emissions followed by acenaphthylene and phenanthrene. Fluorene, anthracene, fluoranthene and pyrene composed a much smaller portion of the PAH emissions.

Tests 3-4 (6/12/09)

Table 3-6 and Table 3-7 summarize the results for Test 3 and Test 4 and the QA/QC results, respectively. The total PAH EF was 8.16 mg/kg for test 3. 70% of emissions are attributed to naphthalene. Acenaphthylene and phenanthrene each contributed to 10% of emissions, respectively. Test 4, which used whole sugarcane stalks, exhibited the highest PAH EF—11.91 mg/kg. Emissions were dominated by naphthalene, acenaphthylene and phenanthrene, similar to all other experiments.

Test 5 (1/27/10)

Two parallel samples were collected in Test 5, which burned whole sugarcane stalks. Table 3-8 summarizes the PAH concentrations and EFs determined for this experiment. Table 3-9 displays the QA/QC results. The total PAH EF was 6.32 ± 0.65 mg/kg, which is similar to the dry leaf experiments and significantly lower than the other whole leaf experiment (Test 4). Although Test 5 exhibited the highest pollutant concentrations of all experiments, the EFs were lower due to the shorter experimental time (indicating denser fuel loading and quicker combustion conditions). Numerous heavier molecular weight compounds, which were not detected in previous experiments, were quantifiable in this test. Compared to the previous experiments, naphthalene contributed less to the total PAH EF (average 59%) and the contribution from heavier molecular weight compounds, such as fluoranthene and pyrene, was increased.

Carbonyls

Five carbonyl experiments were conducted. Three experiments (Tests 1-3) used solely dry leaves and two experiments (Tests 4,5) used whole sugarcane stalks. Table 3-10 summarizes the sampling conditions for each experiment. Sample flow rates ranged from 0.027-0.062 ft³/min and the sampling time ranged from 3 to 20 minutes. Most experiments burned 1 kg of dry leaves except test 5, which burned approximately 253 g.

Test 1 (3/31/09)

In Test 1 a field blank, ambient blank, test sample, and breakthrough sample were collected. Table 3-11 summarizes the measured concentrations, MRLs and EFs for test 1. All compounds of interest were below detection limits in the field blank, ambient blank and breakthrough samples. The total carbonyl EF was 178.3 mg/kg and formaldehyde

was the most dominant carbonyl compound accounting for 64% of measured carbonyl emissions. Other compounds detected included acetaldehyde, propionaldehyde and valeraldehyde. Since this experiment revealed that no sampling breakthrough occurred, backup cartridges were not used in subsequent experiments.

Tests 2-4 (5/28/09)

Three experiments were conducted on 5/28/09. Tests 2 and 3 used dry leaves, whereas Test 4 used whole sugarcane stalks. Test 3-12 summarizes the concentrations and EFs for these experiments. The EFs were 186 ± 58.0 mg/kg and 228 ± 7.78 mg/kg for tests 2 and 3, respectively. Test 4 (with whole stalks) exhibited a much higher total EF: 482 ± 15.9 mg/kg. Again formaldehyde was the most abundant compound followed by acetaldehyde.

Test 5 (12/13/09)

In Test 5, whole sugarcane stalks were burned; however, it should be noted that the sugarcane stalks were from a different source than the previously tested stalks (on 5/28/09). Table 3-13 displays the results. Test 5 exhibited the highest EFs of all experiments: 1401.3 ± 166.2 mg/kg. Except for butyraldehyde, all previously detected compounds were present in this test. Crotonaldehyde was also detected, which was below detection limits in previous experiments.

VOCs

A total of 4 VOC experiments were conducted (using dry leaves) during two testing campaigns on 6/1/09 and 9/29/09. Two samples were collected in parallel for each experiment, resulting in 8 total samples. Table 3-14 summarizes the test conditions for each experiment. All experiments burned 300 g of biomass and the sampling time was

around 3 minutes. The results of each experiment are described in the following sections.

Tests 1 & 2 (6/1/09)

Table 3-15 summarizes the measured concentrations and EFs for the samples. The total VOC EF was 26 ± 2.0 mg/kg and 22.6 ± 2.5 mg/kg for Tests 1 and 2, respectively. In all experiments, benzene was the most dominate compound with EFs ranging from 16-18.7 mg/kg followed by toluene with EFs ranging from 3.6-5.2 mg/kg. *m,p*-xylenes and ethylbenzene followed in abundance and styrene and *o*-xylene had the lowest EFs.

All compounds were below the detection limit in the method blank sample. The surrogate compound recovery was excellent ranging from 97-111% and 95-103% for 1,2-dichloroethane-d4 and toluene-d8, respectively. The recovery efficiencies for the LCS also met acceptance limits and are presented in Table 3-16.

Tests 3 & 4 (9/29/09)

Table 3-17 summarizes the results for VOC Tests 3 and 4. Except for toluene, all compounds in the ambient sample were below the detection limits. The total VOC EF was 25.2 ± 3.5 mg/kg and 22.0 ± 1.0 mg/kg for tests 3 and 4, respectively. As in Tests 1 and 2, benzene was the most dominate compound followed by toluene, *m,p*-xylenes, ethylbenzene, *o*-xylene and styrene, in descending order.

All compounds were below the detection limits in the method blank sample. The spike recovery efficiencies met all acceptance limits with recovery efficiencies ranging from 94-102% for 1,2-dichloroethane-d4 and 101-103% for toluene-d8. The LCS was

also within the recovery efficiency acceptance limits. The LCS data is summarized in Table 3-18.

Recovery Study

A sample was collected on 11/23/09 from a spiked canister containing sample gas with the target compounds in known concentrations. The sample was analyzed on 11/24/09, to be consistent with the average sample storage time of our experiments. The spiked concentration, measured concentration, and % recovery are shown in Table 3-19. As can be seen from this test, the recovery of the target compounds is rather low, especially for heavier molecular weight compounds like styrene, which had a recovery efficiency of only 51%.

The results of this recovery study imply that EPA method 18 may not be an accurate method for the compounds of interest in this study, even when proper protocols are followed, because of significant sample losses during storage and transport. Compounds may be lost to the bag surface or undergo chemical reactions and transformation from the time of collection to analysis. It should be noted that the VOC EFs presented in this study probably underestimate the true EFs.

PM_{2.5}

Mass EFs

Five PM sampling experiments were conducted. Three experiments (Tests 1-3) sampled filterable and condensable PM together. Tests 4 and 5 sampled only the filterable PM (without the impinger train). Table 3-20 summarizes the sampling conditions for all ambient and test PM experiments.

Table 3-21 displays the analytical results for all PM experiments. Note that laboratory blank samples were collected independently of ambient blank samples. Filterable PM EFs were not determined for the 10/3/09 (acetone rinses could not be quantified) and 10/10/09 experiments (filter was too damaged to post weigh). However, the October 2009 experiments and 1/14/10 experiment were used to evaluate the contribution of CPM to the total PM mass. A t-test was performed to compare the blank and test samples with respect to the condensable PM mass. The results show that the condensable PM mass is not statistically higher in the test samples compared to the blank measurements (p value=0.2673). Therefore, it was concluded that the CPM fraction would not significantly contribute to the PM EF and was thus excluded from the PM EF calculation. Ambient blank PM concentrations were subtracted from sample PM concentrations when calculating the EFs. PM EFs ranged from 1.6 g/kg to 3.17 g/kg.

EC and OC EFs

Three samples were collected for EC and OC analysis. In addition, a laboratory blank and one ambient sample (per experiment day) were analyzed. Table 3-22 summarizes the experimental conditions.

Table 3-23 summarizes the analytical results and EFs. OC adsorption on to filters, resulting in a positive artifact, is a documented occurrence (Dhammapala et al., 2007a), which was observed in this experiment by the presence of OC in the laboratory blank and ambient blank samples. To correct for this artifact, ambient OC concentrations were subtracted from the measured OC concentration when determining the OC EF. OC EFs ranged from 0.15-0.35 g/kg and were lower than EC EFs (range: 0.71-0.93 g/kg).

Table 3-1. PAH experiment sampling conditions

Date	Sample ID	Percent isokinetic	Time (min)	Sample volume (ft ³)	Average stack temp. (°F)	Q _{chamber} (ft ³ /min)	m _{burned} (kg)
5/14/09	Ambient-1	101	30.00	14.5	74	225	0.0
	Test-1	94	29.45	9.4	388	183	3.6
5/27/09	Ambient-1	82	30.00	12.4	75	237	0.0
	Test-2a	88	37.58	11.4	392	162	4.0
	Test-2b	88	37.58	9.7	392	162	4.0
6/12/09	Ambient-3/4	91	40.05	17.4	86	225	0.0
	Test-3	88	58.77	11.1	353	188	6.0
	Test-4	97	68.15	13.6	400	186	8.9
1/29/10	Ambient-5	97	32.00	18.5	69	152	0.0
	Field Blank-5	NA	NA	0.0	NA	NA	NA
	Test-5a	102	28.57	11.3	466	131	8.6
	Test-5b	102	28.57	11.9	466	131	8.6

Table 3-2. Test 1 PAH concentrations and EFs

Sample ID	Compound	Concentration (µg/ft ³)	MRL (µg/ft ³)	EF (mg/kg)
Ambient-1	Naphthalene	ND	0.340	NA
	All (excluding naphthalene)	ND	0.034	NA
Test-1	Naphthalene	2.72	0.540	4.05
	Acenaphthylene	0.44	0.054	0.66
	Fluorene	0.13	0.054	0.20
	Phenanthrene	0.39	0.054	0.58
	Anthracene	0.07	0.054	0.10
	Fluoranthene	0.12	0.054	0.18
	Pyrene	0.11	0.054	0.16

Table 3-3. Test 1 QA/QC results

Compound	% Recovery		
	LCS	DLCS	Test-1
Naphthalene	81	83	NA
Acenaphthylene	80	84	NA
Acenaphthene	85	91	NA
Fluorene	92	100	NA
Phenanthrene	93	97	NA
Anthracene	90	94	NA
Fluoranthene	107	107	NA
Pyrene	107	107	NA
Benz[a]anthracene	105	103	NA
Chrysene	98	99	NA
Benzo[b]fluoranthene	114	115	NA
Benzo[k]fluoranthene	105	114	NA
Benzo[a]pyrene	105	104	NA
Indeno[1,2,3- <i>cd</i>]pyrene	114	115	NA
Dibenz[a,h]anthracene	116	116	NA
Benzo[g,h,i]perylene	121	121	NA
Fluorene-d10	100	102	100
Pyrene-d10	115	115	116

Table 3-4. Test 2 PAH concentrations and EFs

Sample ID	Compound	Concentration ($\mu\text{g}/\text{ft}^3$)	MRL ($\mu\text{g}/\text{ft}^3$)	EF (mg/kg)
Ambient-2	Naphthalene	ND	0.400	NA
	All (excluding naphthalene)	ND	0.040	NA
Test-2a	Naphthalene	3.00	0.450	4.56
	Acenaphthylene	0.54	0.045	0.82
	Fluorene	0.18	0.045	0.27
	Phenanthrene	0.52	0.045	0.80
	Anthracene	0.11	0.045	0.17
	Fluoranthene	0.14	0.045	0.21
	Pyrene	0.12	0.045	0.19
Test-2b	Naphthalene	3.25	0.510	4.95
	Acenaphthylene	0.56	0.051	0.85
	Fluorene	0.21	0.051	0.32
	Phenanthrene	0.50	0.051	0.76
	Anthracene	0.10	0.051	0.15
	Fluoranthene	0.13	0.051	0.20
	Pyrene	0.11	0.051	0.17

Table 3-5. Test 2 QA/QC results

Compound	% Recovery			
	LCS	DLCS	Test-2a	Test-2b
Naphthalene	77	80	NA	NA
Acenaphthylene	73	80	NA	NA
Acenaphthene	79	84	NA	NA
Fluorene	83	91	NA	NA
Phenanthrene	87	96	NA	NA
Anthracene	82	92	NA	NA
Fluoranthene	99	107	NA	NA
Pyrene	102	108	NA	NA
Benz[<i>a</i>]anthracene	99	102	NA	NA
Chrysene	96	99	NA	NA
Benzo[<i>b</i>]fluoranthene	109	109	NA	NA
Benzo[<i>k</i>]fluoranthene	114	114	NA	NA
Benzo[<i>a</i>]pyrene	103	106	NA	NA
Indeno[1,2,3- <i>cd</i>]pyrene	107	112	NA	NA
Dibenz[<i>a,h</i>]anthracene	112	111	NA	NA
Benzo[<i>g,h,i</i>]perylene	114	115	NA	NA
Fluorene-d10	99	107	103	97
Pyrene-d10	118	128	125	122

Table 3-6. Tests 3 and 4 PAH concentrations and EFs

Sample ID	Compound	Concentration ($\mu\text{g}/\text{ft}^3$)	MRL ($\mu\text{g}/\text{ft}^3$)	EF (mg/kg)
Ambient-3.4	Naphthalene	ND	0.250	NA
	All (excluding naphthalene)	ND	0.025	NA
Test-3	Naphthalene	3.12	0.450	5.74
	Acenaphthylene	0.43	0.045	0.80
	Fluorene	0.14	0.045	0.27
	Phenanthrene	0.43	0.045	0.80
	Anthracene	0.08	0.045	0.15
	Fluoranthene	0.12	0.045	0.22
	Pyrene	0.10	0.045	0.19
Test-4	Naphthalene	5.67	0.370	8.07
	Acenaphthylene	0.80	0.037	1.14
	Acenaphthene	0.08	0.037	0.11
	Fluorene	0.35	0.037	0.50
	Phenanthrene	0.80	0.037	1.13
	Anthracene	0.15	0.037	0.22
	Fluoranthene	0.21	0.037	0.30
	Pyrene	0.18	0.037	0.26
	Benz[a]anthracene	0.05	0.037	0.07
Chrysene	0.07	0.037	0.10	

Table 3-7. Tests 3 and 4 QA/QC results

Compound	% Recovery				
	LCS	DLCS	Test-3	Test-4	
Naphthalene	75	77	NA	NA	
Acenaphthylene	73	78	NA	NA	
Acenaphthene	82	86	NA	NA	
Fluorene	87	90	NA	NA	
Phenanthrene	94	96	NA	NA	
Anthracene	82	85	NA	NA	
Fluoranthene	98	100	NA	NA	
Pyrene	98	99	NA	NA	
Benz[a]anthracene	92	94	NA	NA	
Chrysene	89	94	NA	NA	
Benzo[b]fluoranthene	78	79	NA	NA	
Benzo[k]fluoranthene	103	107	NA	NA	
Benzo[a]pyrene	99	99	NA	NA	
Indeno[1,2,3-cd]pyrene	99	96	NA	NA	
Dibenz[a,h]anthracene	98	98	NA	NA	
Benzo[g,h,i]perylene	102	101	NA	NA	
Fluorene-d10	83	84		83	84
Pyrene-d10	95	97		94	90

Table 3-8. Test 5 PAH concentrations and EFs

Sample ID	Compound	Concentration ($\mu\text{g}/\text{ft}^3$)	MRL ($\mu\text{g}/\text{ft}^3$)	EF (mg/kg)
Ambient-5	Naphthalene	ND	0.270	NA
	All (excluding naphthalene)	ND	0.027	NA
Field Blank-5	All	ND	NA	NA
Test-5a	Naphthalene	9.07	0.450	3.94
	Acenaphthylene	1.65	0.045	0.71
	Fluorene	0.39	0.045	0.17
	Phenanthrene	1.92	0.045	0.83
	Anthracene	0.29	0.045	0.13
	Fluoranthene	0.79	0.045	0.34
	Pyrene	0.73	0.045	0.32
	Benz[<i>a</i>]anthracene	0.12	0.045	0.05
	Chrysene	0.17	0.045	0.07
	Benzo[<i>b</i>]fluoranthene	0.14	0.045	0.06
	Benzo[<i>k</i>]fluoranthene	0.09	0.045	0.04
	Benzo[<i>a</i>]pyrene	0.09	0.045	0.04
	Indeno[1,2,3- <i>cd</i>]pyrene	0.07	0.045	0.03
	Benzo[<i>g,h,i</i>]perylene	0.07	0.045	0.03
Test-5b	Naphthalene	8.56	0.420	3.72
	Acenaphthylene	1.27	0.042	0.55
	Fluorene	0.31	0.042	0.13
	Phenanthrene	1.46	0.042	0.63
	Anthracene	0.23	0.042	0.10
	Fluoranthene	0.55	0.042	0.24
	Pyrene	0.51	0.042	0.22
	Benz[<i>a</i>]anthracene	0.09	0.042	0.04
	Chrysene	0.13	0.042	0.06
	Benzo[<i>b</i>]fluoranthene	0.13	0.042	0.05
	Benzo[<i>k</i>]fluoranthene	0.07	0.042	0.03
	Benzo[<i>a</i>]pyrene	0.07	0.042	0.03
	Indeno[1,2,3- <i>cd</i>]pyrene	0.06	0.042	0.02
	Benzo[<i>g,h,i</i>]perylene	0.06	0.042	0.03

Table 3-9. Test 5 QA/QC results

Compound	% Recovery			
	LCS	DLCS	Test-5a	Test-5b
Naphthalene	73	66	NA	NA
Acenaphthylene	67	66	NA	NA
Acenaphthene	73	67	NA	NA
Fluorene	75	71	NA	NA
Phenanthrene	84	77	NA	NA
Anthracene	79	76	NA	NA
Fluoranthene	86	79	NA	NA
Pyrene	84	78	NA	NA
Benz[<i>a</i>]anthracene	90	88	NA	NA
Chrysene	93	91	NA	NA
Benzo[<i>b</i>]fluoranthene	95	90	NA	NA
Benzo[<i>k</i>]fluoranthene	98	98	NA	NA
Benzo[<i>a</i>]pyrene	96	92	NA	NA
Indeno[1,2,3- <i>cd</i>]pyrene	100	95	NA	NA
Dibenz[<i>a,h</i>]anthracene	99	94	NA	NA
Benzo[<i>g,h,i</i>]perylene	97	92	NA	NA
Fluorene-d10	78	73	52	70
Pyrene-d10	83	76	63	75

Table 3-10. Carbonyl experiment sampling conditions

Date	Sample ID	Time (min)	Sample volume (ft ³)	Average stack temperature (°F)	Q _{chamber} (ft ³ /min)	m _{burned} (kg)
3/31/09	Ambient-1	20.00	0.840	81	234	0
	Field Blank-1	20.00	0	NA	NA	NA
5/28/09	Test-1	10.00	0.376	353	190	1.00
	Test-1 (breakthrough)	10.00	0.376	353	190	1.00
	Ambient-2/3/4	10.00	0.418	77	195	0
	Test-2a	12.32	0.560	268	178	1.00
	Test-2b	12.32	0.640	268	178	1.00
	Test-3a	10.07	0.430	313	174	1.00
	Test-3b	10.07	0.480	313	174	1.00
	Test-4a	3.18	0.087	600	144	1.09
	Test-4b	3.18	0.078	600	144	1.09
	12/13/09	Ambient-5	5.00	0.309	72	253
Field Blank-2		0.00	0	NA	NA	NA
Test-5a		3.80	0.151	145	227	0.253
Test-5b		3.80	0.103	145	227	0.253

Table 3-11. Test 1 carbonyl concentrations and EFs

Sample ID	Compound	Concentration (µg/m ³)	MRL (µg/m ³)	EF (mg/kg)
Ambient-1	All	ND	13	NA
Field Blank-1	All	ND	NA	NA
Test-1	Formaldehyde	2100	28	113.4
	Acetaldehyde	950	28	51.1
	Propionaldehyde	210	28	11.3
	Valeraldehyde	43	28	2.3
Test-1 (breakthrough)	All	ND	28	NA

Table 3-12. Tests 2,3,4 carbonyl concentrations and EFs

Sample ID	Compound	Concentration ($\mu\text{g}/\text{m}^3$)	MRL ($\mu\text{g}/\text{m}^3$)	EF (mg/kg)
Ambient- 2/3/4	All	ND	25	NA
Test-2a	Formaldehyde	2700	19	184.7
	Acetaldehyde	620	19	42.4
	Valeraldehyde	ND	19	NA
Test-2b	2,5-Dimethylbenzaldehyde	150	19	10.3
	Formaldehyde	1700	17	116.3
	Acetaldehyde	400	17	27.4
Test-3a	Valeraldehyde	20	17	1.4
	Formaldehyde	3100	25	154.6
	Acetaldehyde	1300	25	64.8
	Propionaldehyde	240	25	12.0
	Benzaldehyde	44	25	2.2
Test-3b	Valeraldehyde	53	25	2.6
	Formaldehyde	3600	22	179.5
	Acetaldehyde	760	22	37.9
	Propionaldehyde	30	22	1.5
	Benzaldehyde	ND	22	NA
Test-4a	Valeraldehyde	75	22	3.7
	2,5-Dimethylbenzaldehyde	810	22	40.4
	Formaldehyde	23000	120	275.3
	Acetaldehyde	14000	120	167.6
	Propionaldehyde	1900	120	22.7
	Butyraldehyde	310	120	3.7
	Benzaldehyde	690	120	8.3
Test-4b	Valeraldehyde	140	120	1.7
	2,5-Dimethylbenzaldehyde	1200	120	14.4
	Formaldehyde	20000	140	239.4
	Acetaldehyde	12000	140	143.6
	Propionaldehyde	2000	140	23.9
	Butyraldehyde	ND	140	NA
	Benzaldehyde	870	140	10.4
Valeraldehyde	200	140	2.4	
	2,5-Dimethylbenzaldehyde	4300	140	51.5

Table 3-13. Test 5 carbonyl concentrations and EFs

Sample ID	Compound	Concentration ($\mu\text{g}/\text{m}^3$)	MRL ($\mu\text{g}/\text{m}^3$)	EF (mg/kg)
Ambient-5	All	ND	34	NA
Field Blank-5	All	ND	NA	NA
Test-5a	Formaldehyde	9000	70	873.9
	Acetaldehyde	5600	70	543.8
	Propionaldehyde	680	70	66.0
	Benzaldehyde	81	70	7.9
	Crotonaldehyde, Total	280	70	27.2
Test-5b	Formaldehyde	7300	100	708.9
	Acetaldehyde	4500	100	437.0
	Propionaldehyde	940	100	91.3
	Benzaldehyde	120	100	11.7
	Crotonaldehyde, Total	360	100	35.0

Table 3-14. VOC experiment sampling conditions

Date	Sample ID	Time (min)	Average stack temperature ($^{\circ}\text{F}$)	Q_{chamber} (ft^3)	m_{burned} (kg)
6/1/09	Ambient-1/2a	3.00	88	194	0.0
	Ambient-1/2b	3.00	88	194	0.0
	Test-1a	2.98	252	221	0.3
	Test-1b	2.98	252	221	0.3
	Test-2a	2.85	253	198	0.3
	Test-2b	2.85	253	198	0.3
9/29/09	Ambient-3/4	3.00	84	200	0.0
	Test-3a	3.28	284	140	0.3
	Test-3b	3.28	284	140	0.3
	Test-4a	3.13	290	139	0.3
	Test-4b	3.13	290	139	0.3

Table 3-15. Tests 1 and 2 VOC concentrations and EFs

Sample ID	Compound	Concentration ($\mu\text{g}/\text{m}^3$)	MRL ($\mu\text{g}/\text{m}^3$)	EF (mg/kg)
Ambient-1/2a	Benzene, toluene, ethylbenzene, styrene, <i>o</i> -xylene	ND	5	NA
	<i>m,p</i> -xylenes	ND	10	NA
Ambient-1/2b	Benzene, toluene, ethylbenzene, styrene, <i>o</i> -xylene	ND	5	NA
	<i>m,p</i> -Xylenes	ND	10	NA
Test-1a	Benzene	310	5	17.0
	Toluene	95	5	5.2
	Ethylbenzene	14	5	0.8
	<i>m,p</i> -xylenes	17	10	0.9
	Styrene	5.3	5	0.3
	<i>o</i> -xylene	5.4	5	0.3
Test-1b	Benzene	340	5	18.6
	Toluene	110	5	6.0
	Ethylbenzene	16	5	0.9
	<i>m,p</i> -xylenes	20	10	1.1
	Styrene	6.1	5	0.3
	<i>o</i> -xylene	6.2	5	0.3
Test-2a	Benzene	350	5	18.6
	Toluene	82	5	4.4
	Ethylbenzene	14	5	0.7
	<i>m,p</i> -xylenes	11	10	0.6
	Styrene	ND	5	ND
	<i>o</i> -xylene	ND	5	ND
Test-2b	Benzene	300	5	16.0
	Toluene	67	5	3.6
	Ethylbenzene	11	5	0.6
	<i>m,p</i> -xylenes	ND	10	ND
	Styrene	13	5	0.7
	<i>o</i> -xylene	ND	5	ND

Table 3-16. Tests 1 and 2 LCS % recoveries

Compound	% recovery	Acceptance limit
Benzene	88	68-122
Toluene	84	74-119
Ethylbenzene	88	76-120
<i>m,p</i> -xylenes	89	75-120
Styrene	98	78-124
<i>o</i> -xylene	89	76-121

Table 3-17. Tests 3 and 4 VOC concentrations and EFs

Sample ID	Compound	Concentration ($\mu\text{g}/\text{m}^3$)	MRL ($\mu\text{g}/\text{m}^3$)	EF (mg/kg)
Ambient-3/4	Benzene,			
	ethylbenzene,			
	styrene, <i>o</i> -xylene	ND	5	NA
	<i>m,p</i> -xylenes	ND	10	NA
	Toluene	9.2	5	ND
Test-3a	Benzene	410	5	17.8
	Toluene	160	5	6.5
	Ethylbenzene	25	5	1.1
	<i>m,p</i> -xylenes	31	10	1.3
	Styrene	9.6	5	0.4
	<i>o</i> -xylene	11	5	0.5
Test-3b	Benzene	350	5	15.2
	Toluene	130	5	5.2
	Ethylbenzene	19	5	0.8
	<i>m,p</i> -xylenes	24	10	1.0
	Styrene	ND	5	ND
	<i>o</i> -xylene	8.2	5	0.4
Test-4a	Benzene	330	5	13.6
	Toluene	130	5	5.0
	Ethylbenzene	17	5	0.7
	<i>m,p</i> -xylenes	27	10	1.1
	Styrene	ND	5	ND
	<i>o</i> -xylene	9.3	5	0.4
Test-4b	Benzene	360	5	14.8
	Toluene	150	5	5.8
	Ethylbenzene	21	5	0.9
	<i>m,p</i> -xylenes	34	10	1.4
	Styrene	ND	5	ND
	<i>o</i> -xylene	12	5	0.5

Table 3-18. Tests 3 and 4 LCS % recoveries

Compound	% recovery	Acceptance limits
Benzene	79	68-122
Toluene	84	74-119
Ethylbenzene	85	76-120
<i>m,p</i> -xylenes	85	75-120
Styrene	90	78-124
<i>o</i> -xylene	87	76-121

Table 3-19. Recovery study results

Compound	Spiked concentration ($\mu\text{g}/\text{m}^3$)	Measured concentration ($\mu\text{g}/\text{m}^3$)	% recovery
Benzene	212	170	80
Toluene	216	170	79
Ethylbenzene	212	170	80
<i>m,p</i> -xylenes	416	310	75
Styrene	214	110	51
<i>o</i> -xylene	212	150	71

Table 3-20. PM experiment sampling conditions

Date	Sample ID	% iso-kinetic	Time (min)	Sample volume (ft ³)	Average stack temp. (°F)	Q _{chamber} (ft ³ /min)	m _{burned} (kg)
10/3/09	Ambient-1	155	10.0	5.437	88	164	0
	Test 1	111	7.6	2.806	440	156	1
10/10/09	Ambient-2	81	8.1	5.453	87	250	0
	Test-2	96	7.0	2.468	317	168	1
1/14/10	Ambient-3	96	39.1	17.205	76	175	0
	Test-3	85	17.7	10.886	381	152	2.384
1/27/10	Ambient-4	111	5.0	2.022	66	212	0
	Test-4	86	2.1	1.358	391	145	0.486
2/17/10	Ambient-5/6	111	5.0	2.095	64	145	0
	Test-5	93	1.1	0.638	280	127	0.271
	Tes-6	113	1.0	0.631	284	116	0.201

Table 3-21. PM concentrations and EFs

Date/test	Total filterable PM mass (g)	Filterable PM concentration (g/ft ³)	Total CPM mass (g)	CPM concentration (g/ft ³)	PM EF (g/kg)
10/3/09 Test	3.35E-03	1.19E-03	2.13E-02	7.60E-03	NA
10/10/09 Test	NA	NA	2.57E-02	1.04E-02	NA
11/5/09 Lab Blank	NA	NA	2.28E-02	NA	NA
11/10/09 Lab Blank	NA	NA	1.58E-02	NA	NA
1/14/10 Lab Blank	NA	NA	1.02E-02	5.95E-04	NA
1/14/10 Ambient	1.08E-03	6.28E-05	NA	NA	NA
1/14/10 Test	2.70E-02	2.48E-03	1.82E-02	7.28E-04	2.73
1/27/10 Ambient	1.39E-03	6.87E-04	NA	NA	NA
1/27/10 Test	7.71E-03	5.68E-03	NA	NA	3.17
2-17-10 Ambient	8.60E-04	4.11E-04	NA	NA	NA
2-17-10 Test 1	2.30E-03	3.61E-03	NA	NA	1.60
2-17-10 Test 2	3.07E-03	4.87E-03	NA	NA	2.44

Table 3-22. EC/OC experiment sampling conditions

Sample	Sample date	Sample volume (ft ³)	Average stack temp. (°F)	Q _{chamber} (ft ³ /min)	Sample time (min)	m _{burned} (kg)
Ambient-1	12/10/09	3.99	61	NA	10.00	0
Test-1	12/10/09	1.94	156	207	3.50	0.5
Ambient-2/3	12/11/09	6.09	51	NA	10.00	0
Test-2	12/11/09	2.59	240	187	3.70	0.5
Test-3	12/11/09	2.54	186	207	4.38	0.5

Table 3-23. OC and EC concentrations and EFs

Sample	Concentration on filter		Concentration in air		EFs	
	OC ($\mu\text{g}/2.7\text{ cm}^2$)	EC ($\mu\text{g}/2.7\text{ cm}^2$)	OC ($\mu\text{g}/\text{ft}^3$)	EC ($\mu\text{g}/\text{ft}^3$)	OC (g/kg)	EC (g/kg)
Lab Blank	2.2	0	NA	NA	NA	NA
Ambient-1	6.4	0	12.88	0.00	NA	NA
Test-1	60.6	154.1	250.23	636.16	0.35	0.93
Ambient-2/3	8.4	0	11.04	0.00	NA	NA
Test-2	39.3	176.8	121.41	546.63	0.15	0.76
Test-3	37.4	124.1	118.03	391.20	0.19	0.71

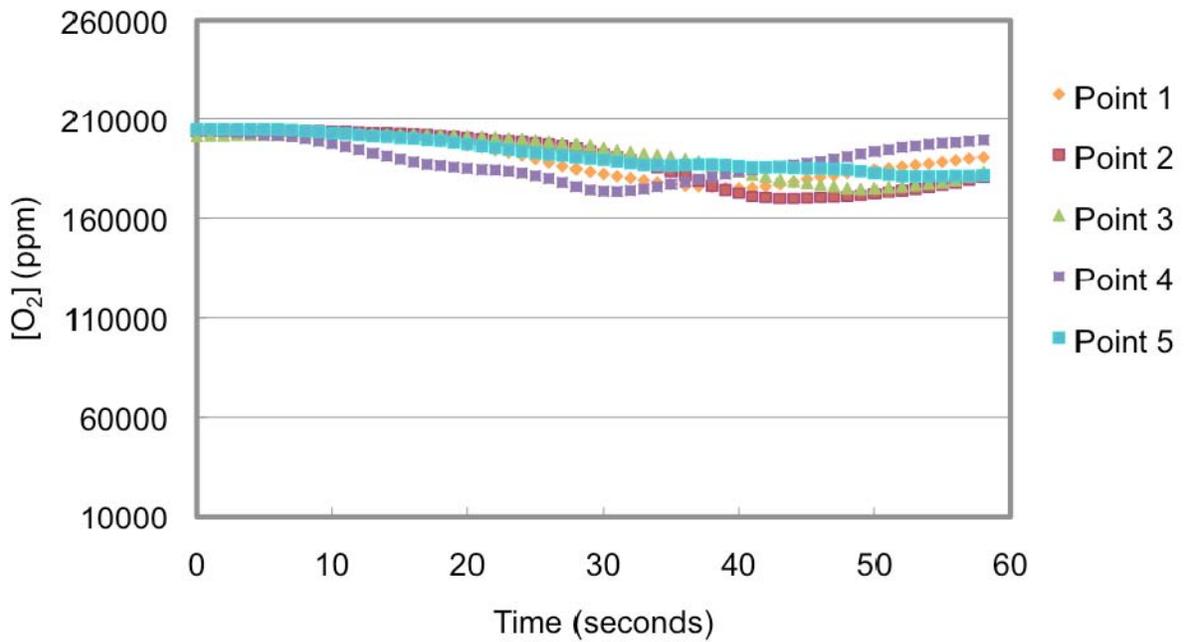


Figure 3-1. Uniformity test data

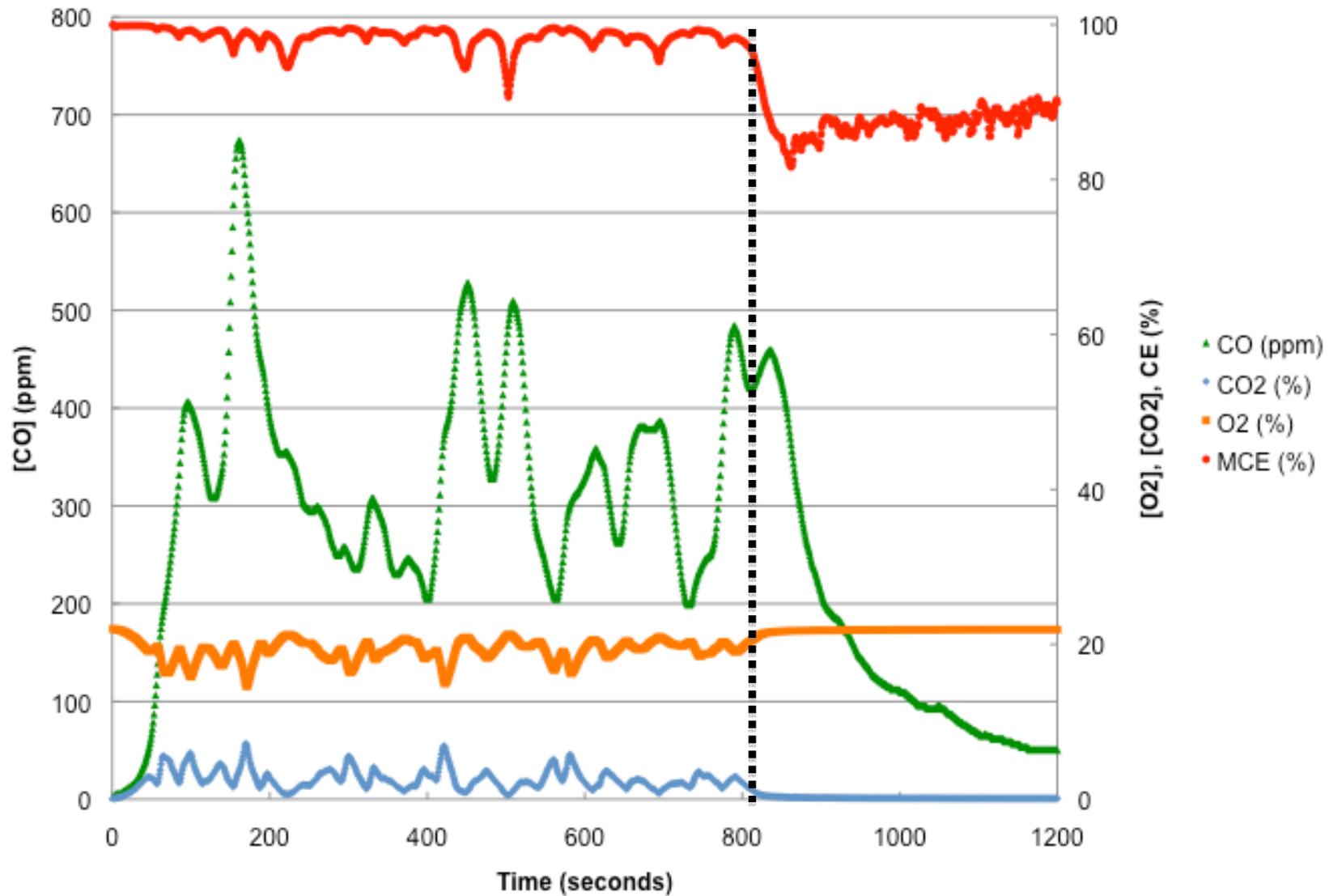


Figure 3-2. Flue gas concentrations and MCE (Note: dashed line represents when the flame was extinguished)

CHAPTER 4 DISCUSSION

EF summary

Table 4-1 summarizes the average and standard deviation of the speciated EFs in addition to the 95% confidence interval (calculated using *t* values) for the dry and whole stalk experiments separately for all the pollutants quantified in this study. A detailed analysis of the emission and trends for each pollutant class are further provided in the following sections.

PAHs

PAH emissions were dominated by lower 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. 3-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. The total PAH EF for dry leaf experiments was 7.13 ± 0.94 mg/kg. This EF does not include any emissions of heavier 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.

Figure 4-1 compares EFs determined in this study to EFs determined by Jenkins et al. (1996b) for all PAH compounds excluding naphthalene, since naphthalene EFs were marked as questionable by Jenkins et al. (1996b) due to high blank concentrations in their QA/QC samples. Figure 4-2 shows a comparison of sugarcane PAH EFs and EFs determined by Hays et al. (2002) for foliar fuels (including naphthalene). It should be noted that Hays et al. (2002) quantified particulate and gaseous PAH compounds

separately; therefore, the figure only compares compounds that are known to exist mainly in the gas-phase (i.e., low molecular weight compounds). Sugarcane EFs are comparable, but lower than Jenkins et al. (1996b) for agricultural residue. The relative abundance of acenaphthylene and phenanthrene is consistent for all fuel types. Hays et al. (2002) PAH EFs are much higher than the EFs determined in this study, but again the abundance of naphthalene and acenaphthylene are consistent between these studies. The lower EFs exhibited in this study are likely due to the high MCE observed in this study (~99%). Since PAH compounds (as well as other pollutant emissions) form as a result of incomplete combustion, it is expected that pollutant emissions will decrease with increasing combustion efficiency.

PAH concentrations in whole stalk experiments were slightly higher than dry leaf experiments. As other studies have demonstrated, MC has an important impact on emissions (Hays et al., 2005; McMeeking et al., 2009; Simoneit, 2002). Generally, higher MCs inhibit ideal 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 very sensitive to temperature—PAH 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 will likely have a lower combustion temperature, possibly inhibiting PAH formation. This may explain why whole stalk PAH EFs were only slightly higher than dry leaf EFs. It is apparent that there are numerous factors that impact emissions, and these impacts are not always straightforward.

As naphthalene consistently comprises a large portion of the PAH emissions, it may serve 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 ($r^2=0.99$), acenaphthylene ($r^2=0.98$) and phenanthrene ($r^2=0.98$) concentrations and the total PAH concentration. Figure 4-3 shows the relationships between individual compound concentrations and the total PAH concentration. The same analysis was performed for individual PAH compound EFs compared to the total PAH EF, and a similar result was found (Figure 4-4). These findings suggest that measuring a few select PAH compounds could infer the total PAH emissions from a particular source, thereby simplifying sampling and analytical procedures.

Organic compounds, like PAHs, can serve as source markers in apportionment studies (Yang et al., 2006; Schauer et al., 2001). Certain compounds can be used as specific tracers (e.g., levoglucosan) or compound ratios or patterns can be used to identify specific sources. A number of helpful ratios were identified in this study, which could serve as source information for future source apportionment studies. The concentration ratio of fluoranthene to pyrene was on average 1.15 in all experiments. The ratio of phenanthrene/acenaphthylene was 1.0 and the ratio of indeno[1,2,3-cd]pyrene/(indeno[1,2,3-cd]pyrene+benzo[ghi]perylene) was 0.475. These ratios as well as some from other studies for other sources are compared in Table 4-2. The

differences between these ratios and the ratios of other sources can be helpful when apportioning emissions to specific sources (Ravindra et al., 2008).

Carbonyls

The mean carbonyl EFs were 231.8 ± 52.3 mg/kg and 909.6 ± 527.7 mg/kg for dry leaf and whole stalk experiments, respectively. In all experiments, formaldehyde was the most dominant carbonyl compound accounting for over 50% (ranged from 51-78%) of quantified carbonyl emissions. Acetaldehyde was the second most abundant compound followed by propionaldehyde. Other compounds detected, in much lower concentrations, were butyraldehyde, benzaldehyde, valeraldehyde and 2,5-dimethylbenzaldehyde. Crotonaldehyde was only detected in the 12/13/09 experiment, which also exhibited the highest EFs.

As with the dominant PAH compounds, formaldehyde and acetaldehyde EFs were highly correlated with the total PAH EF. Figure 4-5 shows the relationships, which had r^2 values of 0.991 and 0.996 for formaldehyde and acetaldehyde, respectively. Figure 4-6 shows the correlations between formaldehyde and acetaldehyde concentrations and the total carbonyl concentration, which also exhibited excellent correlation. Because of their high correlation, formaldehyde and acetaldehyde could serve as predictor compounds for total carbonyl emissions.

EFs from whole stalk experiments exhibited considerably higher EFs for most compounds (except valeraldehyde) than for dry leaf experiments. The ratio of whole stalk EFs to dry stalk EFs ranged from 0.8 (valeraldehyde) to 7.2 (acetaldehyde). The 12/13/09 whole stalk experiment had much higher EFs than the 5/28/09 whole stalk experiment. In addition to the differences in the biomass source (collected at different

times and from different field locations), the two experiments had markedly different burning conditions. The fire of the 5/28/09 experiment was much more intense than the fire of the 12/13/09 experiment. The average temperature of the former was 600 °F and 1 kg of biomass burned in 3 minutes, whereas in the later experiment only 256 g of biomass burned in 3 minutes and the average temperature was around 145 °F. The different burning conditions were a result of different initial loading conditions (i.e., how much sugarcane was initially loaded) and operator differences (i.e., how the researcher fed the biomass into the chamber). The differences in the EFs can be attributed to these differences in the burning conditions. The more intense fire had more complete combustion as compared to the lower temperature fire, which exhibited more smoldering combustion.

The difference between carbonyl whole stalk and dry leaf EFs is more significant than PAH EFs for the two experimental conditions. This can be attributed to the fact that PAH EFs are very sensitive to temperature in addition to CE, whereas carbonyl EFs may be less dependent on temperature. It should also be noted that tests 4 and 5 (for both carbonyls and PAHs) used biomass from different sources. 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.

Figure 4-7 compares the carbonyl EFs to crop residue burned in a cookstove (Zhang et al., 1999) and foliar fuels (Hays et al., 2002). The 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 dominate compounds in all studies.

Hedberg et al. (2002) discussed using the ratio of formaldehyde to acetaldehyde for source characterization. They reported an average ratio of 5 (range: 3.3-8.8) for birch wood burning in a wood stove. In this study the average ratio was 2.7 with a range of 1.6 to 4.7, which is very similar to a ratio of 3 obtained for motor vehicle emissions by Johansson et al. (2001). This highlights that carbonyl compound ratios may not be helpful in identifying emissions from specific sources. It should also be noted that formaldehyde and acetaldehyde compounds are formed in the atmosphere through the photochemical oxidation of organic compounds, further emphasizing that these compounds are not suitable as source markers.

VOCs

First, it should be emphasized that the EFs presented here may underestimate the true EFs because of sampling losses observed. According to the recovery study, the concentrations may be underestimated by approximately 20% for benzene, toluene and ethylbenzene, 25% for *m,p*-xylene, 29% for *o*-xylene and 49% for styrene. Samples loss in Tedlar bags is a documented problem for this type of sampling (Kumar and Viden, 2007).

Overall, the experiments had very consistent results. In all experiments, benzene was the most prominent compound quantified, accounting for an average of 69% (ranged between 63-77%) of emissions. Toluene accounted for an average of 22% (ranged between 17-25%) of VOC emissions. The relative abundance of benzene and toluene as the dominant aromatics is consistent with other biomass combustion studies

(Hays et al., 2002) The other compounds were present in much lower fractions—*m,p*-xylenes, ethylbenzene, *o*-xylene and styrene accounted, on average, for 4%, 3%, 2% and 1% of VOC emissions, respectively. However, it is likely styrene accounts for a larger fraction, but in this experiment it exhibited a significantly lower recovery efficiency as compared to the other compounds.

VOC EFs are significantly lower than those determined by Hays et al. (2002) for foliar fuels, but are similar with those determined by Jenkins et al. (1996a) for almond and walnut prunings. A comparison of the EFs determined in this study and Jenkins et al. (1996a) are presented in Figure 4-8. Yokelson et al. (2008) presented VOC EFs for sugarcane based on one experiment that used proton-transfer reaction mass spectrometry (PTR-MS), a real-time measurement technique. Yokelson et al.'s (2008) VOC EFs significantly higher than the EFs determined in this study and are on par to Hays et al. (2002). Table 4-3 summarizes the comparison.

Hedberg et al. (2002) suggested comparing ratio of toluene to benzene to discriminate between various sources. They found an average ratio of 0.4, which is very similar to the ratio determined in this study—0.32. The low toluene to benzene is quite different from the ratio determined by Johannson et al. (2001) for vehicle exhaust—3.6, which may make this a useful ratio to differentiate between biomass burning and vehicular exhaust emissions in source apportionment studies.

PM_{2.5}

The mean PM_{2.5} EF was 2.49 ± 0.66 g/kg, based on dry leaf experiments. The EF is in excellent agreement with the PM_{2.5} EF for sugarcane determined by Yokelson et al. (2008) and is within the range of the current published PM EF for sugarcane pre-harvest

burning (USEPA, 1995). The sugarcane PM_{2.5} EF also agrees with other biomass materials such as wheat straw (Dhammapala et al., 2007b; Hays et al., 2005) and rabbitbrush (McMeeking et al., 2009), but is lower than EFs determined for rice straw (Hays et al., 2005) and other foliar fuels, which are not presented in Table 4-4 (Hays et al., 2002; McMeeking et al., 2009).

EC and OC

There are a few uncertainties with EC/OC sampling and analysis that should be mentioned. Namely, the OC sampling artifacts and the different methods used for carbon measurements. Accurate OC sampling is complicated by both positive and negative artifacts, which are attributed to OC's volatility. During sampling, some gaseous organic compounds may absorb on the filter surface or onto collected particles, resulting a positive artifact. In contrast, OC particles collected on the filter may vaporize and be lost during sampling or during the storage (negative artifact). Since the sampling time was very short in this study (less than 5 minutes), the magnitude of the negative and positive OC artifacts is expected to be low. However, a definite positive OC artifact was observed from the presence of OC in both the laboratory and ambient blank samples, but was accounted for in determining the OC EF. Different studies account for these artifacts in various ways.

The second uncertainty in OC/EC determinations is the analytical method used. Two methods are currently used: the Interagency Monitoring of Protected Visual Environments (IMPROVE) protocol and NIOSH Method 5040. The methods differ in their temperature profile protocols (i.e., the timing and set points of the heating sequence) and in the technique used to correct for OC that is pyrolyzed into EC during the analytical sequence (IMPROVE method uses reflectance whereas the NIOSH

method uses transmittance). Due to the major differences in these methods, EC and OC concentrations are currently operationally defined by the analytical technique used and results from the two techniques may differ significantly (Chow et al., 2001; McMeeking et al., 2009). The different analytical techniques used should be accounted for when reporting and comparing OC and EC data.

In this study, the average EFs for OC and EC were 0.23 ± 0.102 g/kg and 0.80 ± 0.115 g/kg, respectively. The concentration ratio of OC to EC was 0.31 ± 0.086 and the EF ratio of OC to EC was 0.28 ± 0.086 . The high EC relative to OC ratio found in this study is very unique for biomass burning. OC dominates EC in most biomass burning emissions; however, a few exceptions have been reported (McMeeking et al., 2009). Table 4-5 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) tested 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 EF’s increased with increasing CE, particularly for MCE>93%; however, EC’s dependence on MCE was not as strongly correlated as in the case of OC ($r^2=0.09$). 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 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.

HAP Emission Estimates

The total yearly emissions of the HAPs investigated in this study were estimated based on the EFs determined. The emissions were then compared to the 2005 national emission inventory to estimate the relative importance of this practice to PBC and Florida's emission inventories (USEPA, 2010).

The yearly emissions were calculated assuming 335,650 acres of sugarcane were burned and a fuel loading of 7 tons/acre. Emissions were estimated considering both dry leaf and whole stalk EFs. EFs were taken as the upper limit of the 95% confidence interval for the range of EFs determined for each category. Table 4-6 summarizes the EFs used and the total emissions for each pollutant and Table 4-7 summarizes the contribution of sugarcane field burning to the emission inventories. Tables 1 and 2 only present data for pollutants reported in the national emission inventory, although some other pollutants were studied in this project (e.g., PM_{2.5}).

As shown in Table 4-7, sugarcane field burning did not contribute substantially (<5%) to VOC compounds in PBC, and thus their state contribution was not estimated. VOC emissions were dominated by gasoline sources (on-road and non-road equipment). Sugarcane field burning also did not contribute significantly to naphthalene emissions in PBC and Florida. However, sugarcane field burning contributed substantially to emissions of other PAH compounds and carbonyl compounds.

Based on dry leaf EFs, sugarcane field burning contributions ranged from 44-64% for PBC PAH emissions and 51-56% for carbonyl emissions. Based on whole stalk EFs, sugarcane field burning contributions ranged from 23-78% for PBC PAH emissions and 86-91% for PBC carbonyl compound emissions.

Sugarcane field burning is also an important source for certain PAH and carbonyl compounds in the Florida state emission inventory. On the state level, sugarcane burning (using whole stalk EFs) contributed to over 10% of emissions for acenaphthylene, fluorene, and benzo(b)fluoranthene compounds. Emission contributions for carbonyl compounds were even greater—16, 29 and 37% for formaldehyde, acetaldehyde and propionaldehyde compounds, respectively. Using the dry leaf EFs, contributions range from 1-8% for these compounds.

Since a large amount of biomass is burned in the localized area of PBC and any biomass combustion produces PAH and carbonyl compounds, it is expected that the emissions from this source will be a major contributor to the local emissions.

Table 4-1. EF summary

Compound	Dry leaves		Whole stalks	
	Mean ± std. dev.	95% confidence interval	Mean ± std. dev.	95% confidence interval
PAHs (mg/kg)	7.13±0.94	7.13±1.48	8.18±3.26	8.18±8.10
Naphthalene	4.83±0.72	4.83±1.14	5.24±2.45	5.24±6.10
Acenaphthylene	0.78±0.09	0.78±0.14	0.80±0.30	0.80±0.75
Acenaphthene	ND	NA	0.11	NA
Fluorene	0.26±0.05	0.26±0.08	0.27±0.20	0.27±0.50
Phenanthrene	0.73±0.10	0.73±0.16	0.87±0.25	0.87±0.63
Anthracene	0.14±0.03	0.14±0.05	0.15±0.06	0.15±0.15
Fluoranthene	0.20±0.02	0.20±0.03	0.30±0.05	0.30±0.13
Pyrene	0.18±0.01	0.18±0.02	0.27±0.05	0.27±0.12
Benz[a]anthracene	ND	NA	0.05±0.01	0.05±0.04
Chrysene	ND	NA	0.08±0.02	0.08±0.05
Benzo[b]fluoranthene	ND	NA	0.06±0.00	0.06±0.01
Benzo[k]fluoranthene	ND	NA	0.03±0.01	0.03±0.02

Table 4-1. Continued

Compound	Dry leaves		Whole stalks	
	Mean ± std. dev.	95% confidence interval	Mean ± std. dev.	95% confidence interval
Benzo[a]pyrene	ND	NA	0.04±0.01	0.04±0.01
Indeno[1,2,3- <i>cd</i>]pyrene	ND	NA	0.03±0.00	0.03±0.01
Benzo[<i>g,h,i</i>]perylene	ND	NA	0.03±0.00	0.03±0.01
Carbonyls (mg/kg)	201±38.2	201±47.5	942±539	942±857.3
Formaldehyde	150±33.8	150±42	524±316	524±503
Acetaldehyde	44.8±14.1	44.8±18	323±198	323±316
Propionaldehyde	8.3±5.9	8.3±7.3	51.0±33.6	51.0±53
Butyraldehyde	ND	NA	3.7	NA
Benzaldehyde	2.2	NA	9.6±1.8	9.6±2.8
Valeraldehyde	2.5±1.2	2.5±1.4	2.1±0.5	2.1±0.8
2,5-Dimethylbenzaldehyde	ND	NA	33.0±26.2	33.0±41.7
Crotonaldehyde, Total	ND	NA	31.1±5.5	31.1±8.7
VOCs (mg/kg)	23.9±2.62	23.9±1.89	NA	NA
Benzene	16.5±1.89	16.5±1.58	NA	NA
Toluene	5.2±0.94	5.2±0.79	NA	NA
Ethylbenzene	0.8±0.15	0.8±0.12	NA	NA
<i>m,p</i> -Xylenes	0.9±0.45	0.9±0.38	NA	NA
Styrene	0.3±0.25	0.3±0.21	NA	NA
<i>o</i> -Xylene	0.3±0.19	0.3±0.16	NA	NA
Particulate matter (g/kg)				
PM _{2.5}	2.5±0.66	2.5±1.1	NA	NA
EC	0.23±0.10	0.23±0.26	NA	NA
OC	0.80±0.12	0.80±0.29	NA	NA

Table 4-2. Signature PAH compound ratios

Ratio	Sugarcane burning	Cars ^a	Diesel ^a	Wood burning ^a
Indeno[1,2,3- <i>cd</i>]pyrene/(indeno[1,2,3- <i>cd</i>]pyrene+benzo[<i>ghi</i>]perylene)	0.48	0.18	0.37	0.62
Phenanthrene/acenaphthylene	1.00	NA	NA	NA
Fluoranthene/pyrene	1.15	0.60	NA	NA

^aRavindra et al., 2008

Table 4-3. VOC EF (mg/kg) comparison

Compound	Sugarcane	Sugarcane ^a	Florida palm and slash pine ^b	Wheat ^c
Benzene	16.5	207	168.5	145
Toluene	5.2	120	145.5	77
Elthylbenzene	0.8	60	20.2	NA
<i>m,p</i> -Xylenes	0.9	NA	54.5	NA
Styrene	0.4	NA	19.0	91
<i>o</i> -Xylene	0.3	NA	15.0	NA

^aYokelson et al., 2008, ^bHays et al., 2002, ^cJenkins et al., 1996a

Table 4-4. PM EF (g/kg) comparison

Other references						
Sugarcane PM _{2.5}	Sugarcane PM ^a	Sugarcane PM _{2.5} ^b	Wheat ^c	Wheat straw ^d	Rice straw ^d	Rabbit-brush ^e
2.49 ± 0.66	2.3-3.5	2.17	3.0±0.6	4.71±0.04	12.95±0.30	3.4

^aUSEPA, 1995, ^bYokelson et al., 2008, ^cDhammapala et al., 2007, ^dHays et al., 2005, ^eMcMeeking et al., 2009

Table 4-5. EC and OC EF comparison

	Sugarcane	Other references			
		Wheat ^a	Wheat ^b	Rice ^b	Rabbitbrush ^c
OC (g/kg)	0.23 ± 0.102	1.9±1.1 (CE 94±3.2%)	1.23±0.03	8.94±0.42	0.5 (MCE~95.6%)
EC (g/kg)	0.80 ± 0.115	0.35±0.16 (CE 96±2.1%)	0.52±0.00	0.17±0.04	1.4 (MCE~95.6%)

^aDhammapala et al., 2007 (modified NIOSH), ^bHays et al., 2005 (NIOSH), ^cMcMeeking et al., 2009 (modified NIOSH)

Table 4-6. Emission factors and yearly emissions for sugarcane field burning

Compound	EF (upper 95% confidence limit)		Yearly emissions (tons)	
	Dry leaves	Whole stalks	Dry leaves	Whole stalks
PAHs (mg/kg)				
Naphthalene	5.97	11.34	14.027	26.644
Acenaphthylene	0.92	1.55	2.162	3.642
Acenaphthene	NA	0.11	NA	0.258
Fluorene	0.34	0.77	0.799	1.809
Phenanthrene	0.89	1.50	2.091	3.524
Anthracene	0.19	0.30	0.446	0.705
Fluoranthene	0.23	0.43	0.540	1.010
Pyrene	0.20	0.39	0.470	0.916
Benz[<i>a</i>]anthracene	NA	0.09	NA	0.211
Chrysene	NA	0.13	NA	0.305
Benzo[<i>b</i>]fluoranthene	NA	0.07	NA	0.164
Benzo[<i>k</i>]fluoranthene	NA	0.05	NA	0.117
Benzo[<i>a</i>]pyrene	NA	0.05	NA	0.117
Indeno[1,2,3- <i>cd</i>]pyrene	NA	0.04	NA	0.094
Benzo[<i>g,h,i</i>]perylene	NA	0.04	NA	0.094
Carbonyls (mg/kg)				
Formaldehyde	192.0	1027.0	451.1	2413.0
Acetaldehyde	62.8	639.0	147.6	1501.3
Propionaldehyde	15.6	104.0	36.7	244.4
VOCs (mg/kg)				
Benzene	18.1	NA	42.5	NA
Toluene	6.0	NA	14.1	NA
Elthylbenzene	0.9	NA	2.2	NA
<i>m,p</i> -Xylenes	1.3	NA	3.0	NA
Styrene	0.5	NA	1.2	NA
<i>o</i> -Xylene	0.5	NA	1.1	NA

Table 4-7. Contribution of sugarcane field burning to annual emissions in PBC and Florida

Compound	Contribution to emissions (%)			
	PBC (dry leaves)	PBC (whole stalks)	Florida (dry leaves)	Florida (whole stalks)
PAHs (mg/kg)				
Naphthalene	0.9	1.7	0.7	1.3
Acenaphthylene	56.9	69.0	6.7	10.8
Acenaphthene	NA	52.3	NA	6.2
Fluorene	60.8	77.8	8.3	17.0
Phenanthrene	63.7	74.7	5.9	9.5
Anthracene	58.0	68.6	2.3	3.6
Fluoranthene	54.2	68.9	2.0	3.7
Pyrene	44.2	60.7	1.3	2.5
Benz[<i>a</i>]anthracene	NA	50.1	0.0	1.0
Chrysene	NA	66.6	NA	1.5
Benzo[<i>b</i>]fluoranthene	NA	77.0	NA	11.0
Benzo[<i>k</i>]fluoranthene	NA	61.0	NA	1.4
Benzo[<i>a</i>]pyrene	NA	62.4	0.0	2.1
Indeno[1,2,3- <i>cd</i>]pyrene	NA	53.7	NA	0.9
Benzo[<i>g,h,i</i>]perylene	NA	22.6	NA	0.6
Carbonyls (mg/kg)				
Formaldehyde	53.4	86.0	3.3	15.5
Acetaldehyde	51.2	91.4	3.8	28.7
Propionaldehyde	56.1	89.5	8.0	36.6
VOCs (mg/kg)				
Benzene	3.2	NA	ND	NA
Toluene	0.5	NA	ND	NA
Elthylbenzene	0.4	NA	ND	NA
Styrene	1.6	NA	ND	NA
<i>o,m,p</i> -xylene (mixture)	1.8	NA	ND	NA

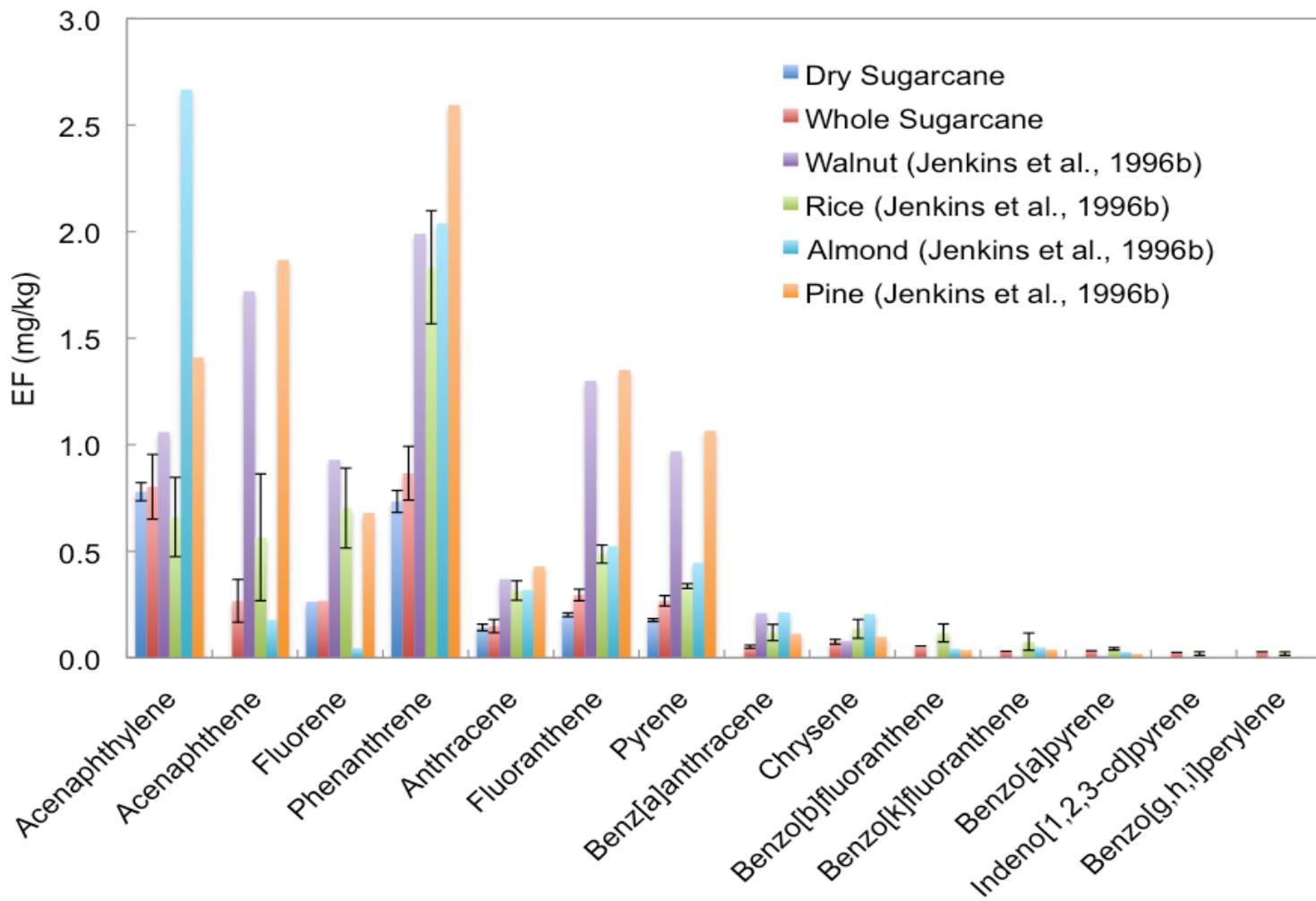


Figure 4-1. Comparison of PAH EFs to Jenkins et al., 1996b

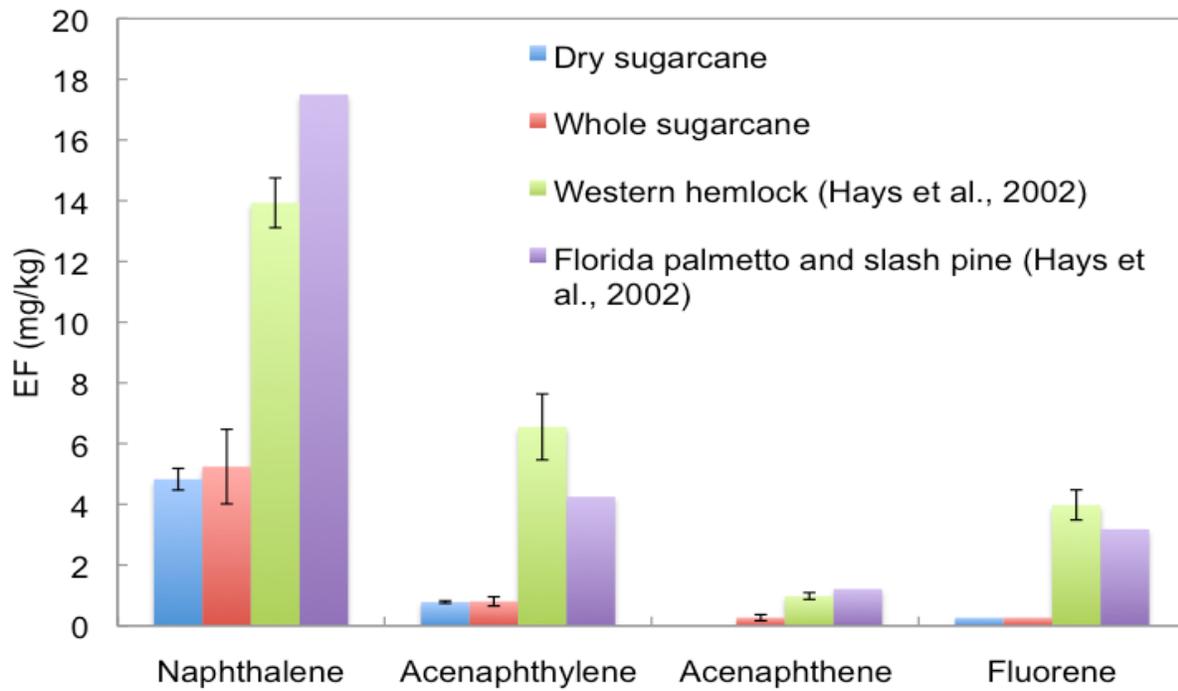


Figure 4-2. Comparison of PAH EFs to Hays et al., 2002

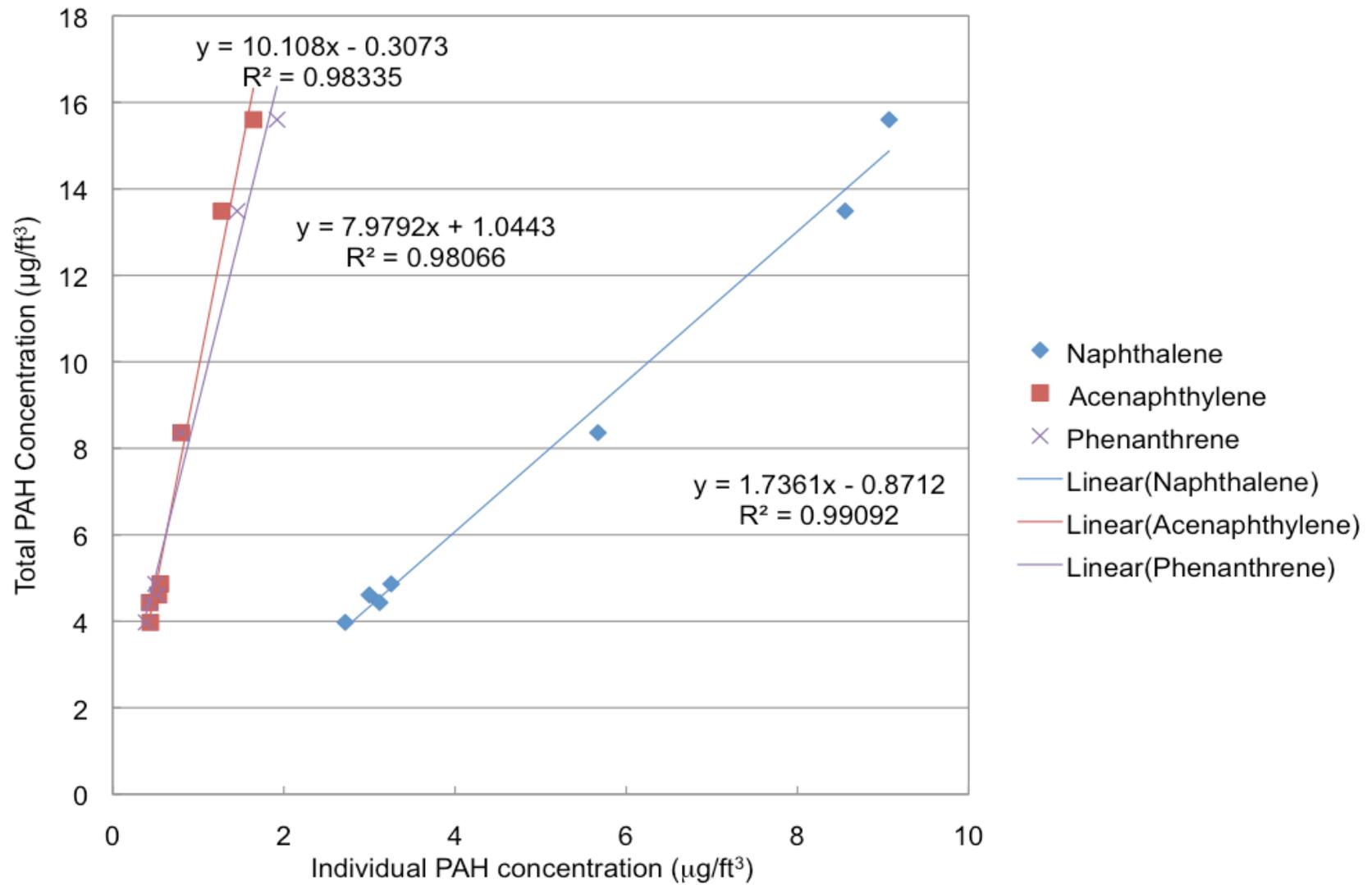


Figure 4-3. Total PAH concentration as a function of individual PAH concentrations

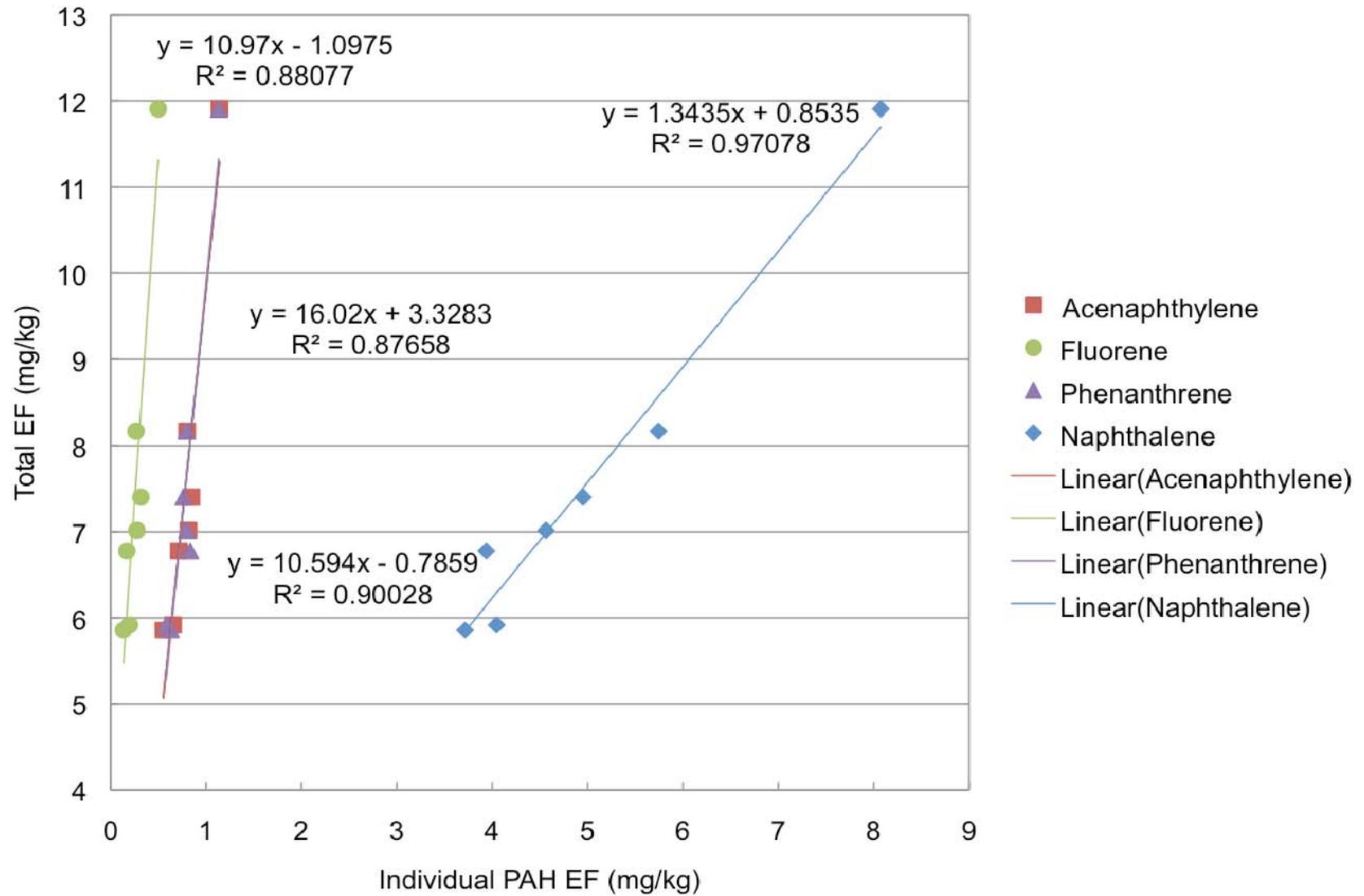


Figure 4-4. Total PAH EF as a function of individual PAH EFs

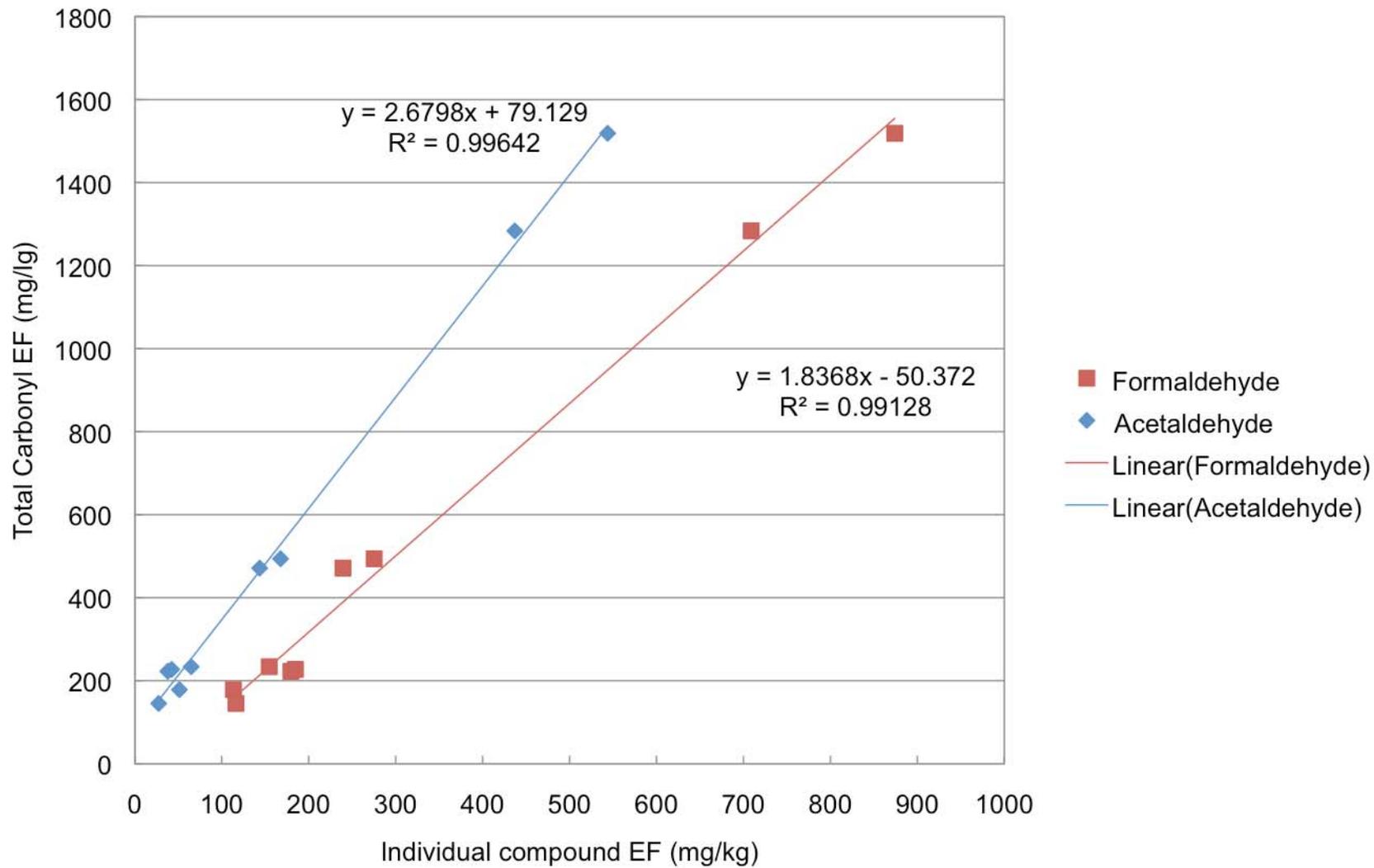


Figure 4-5. Total carbonyl EF as a function of individual carbonyl EFs

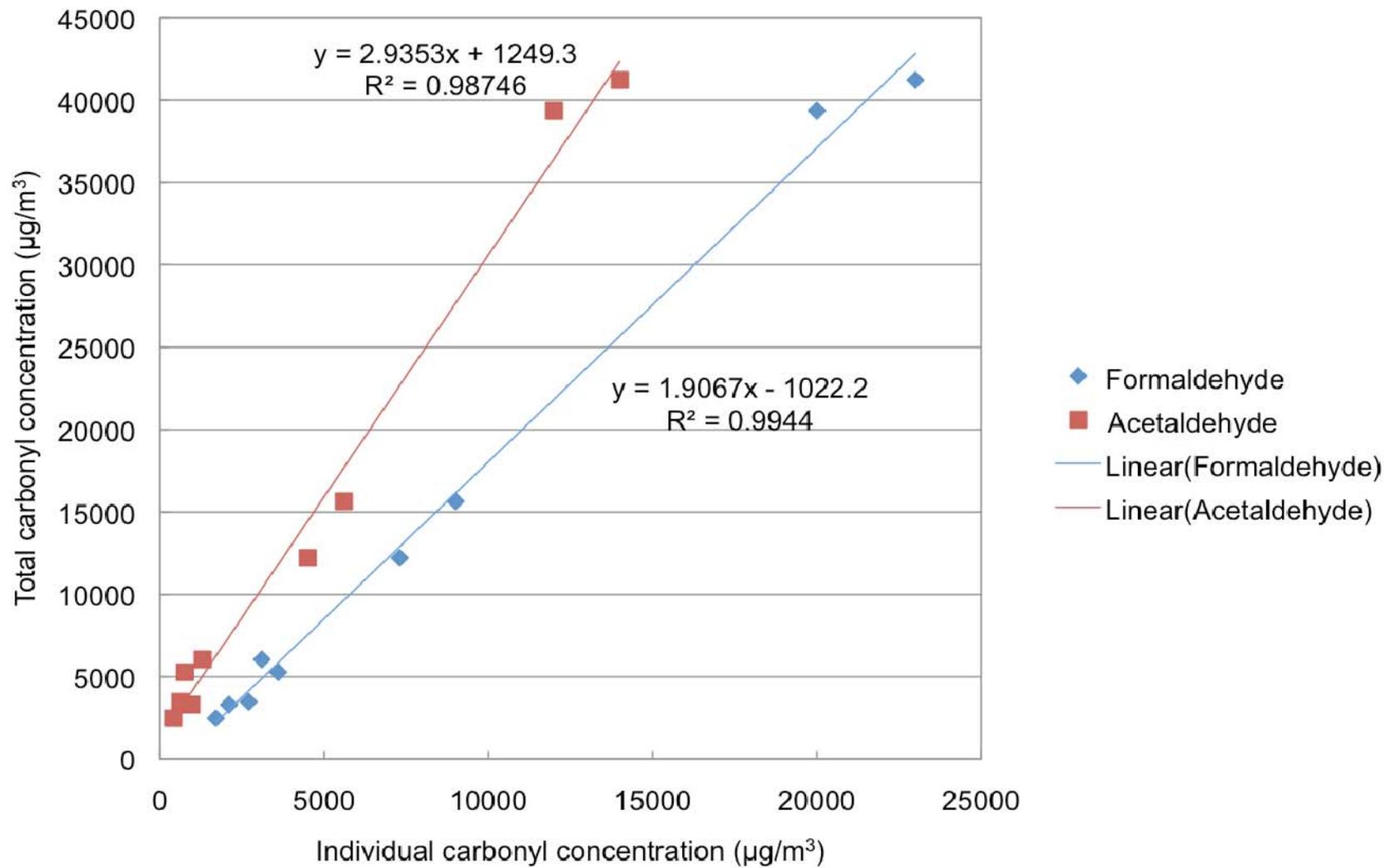


Figure 4-6. Total carbonyl concentration as a function of individual carbonyl concentration

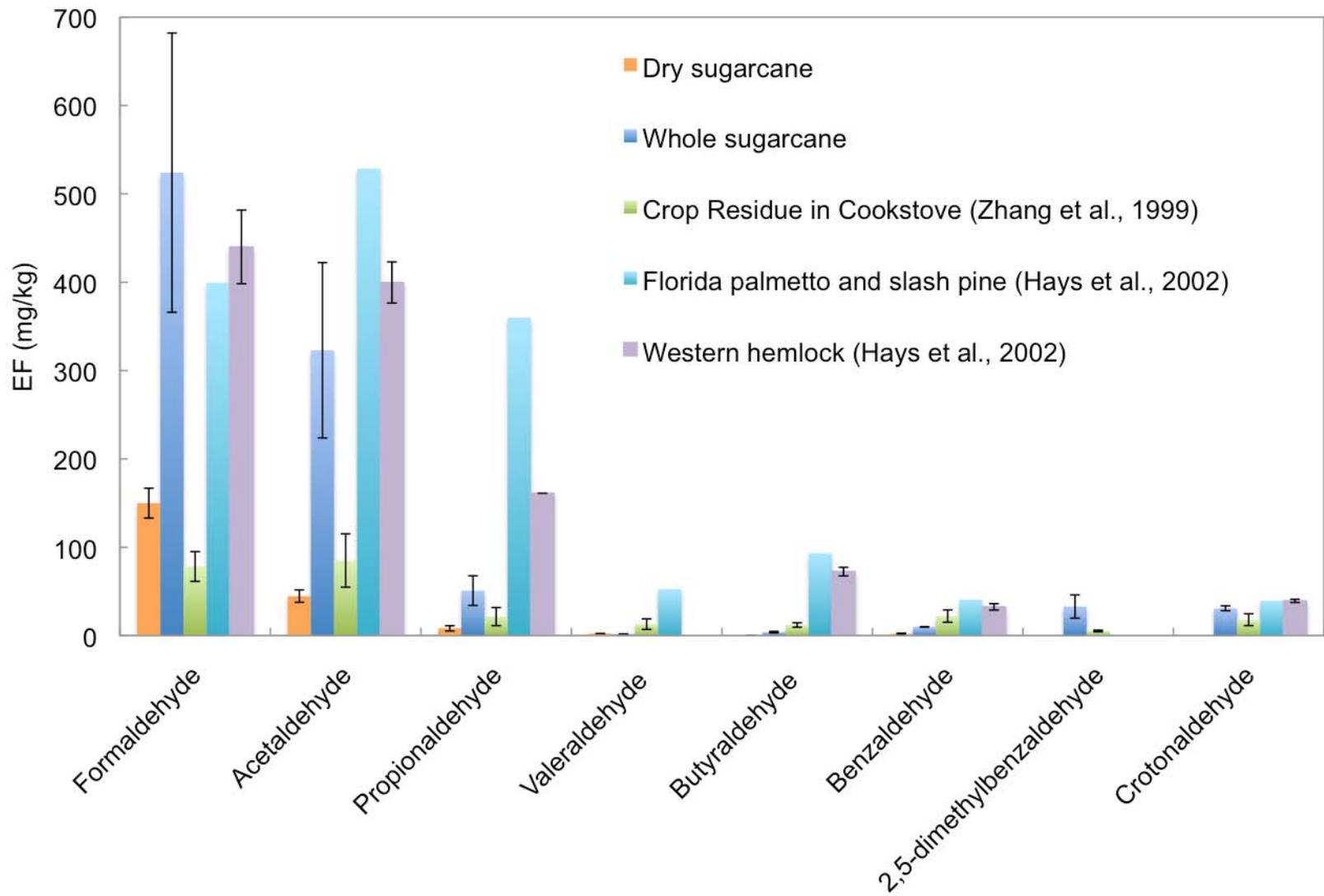


Figure 4-7. Comparison of carbonyl EFs

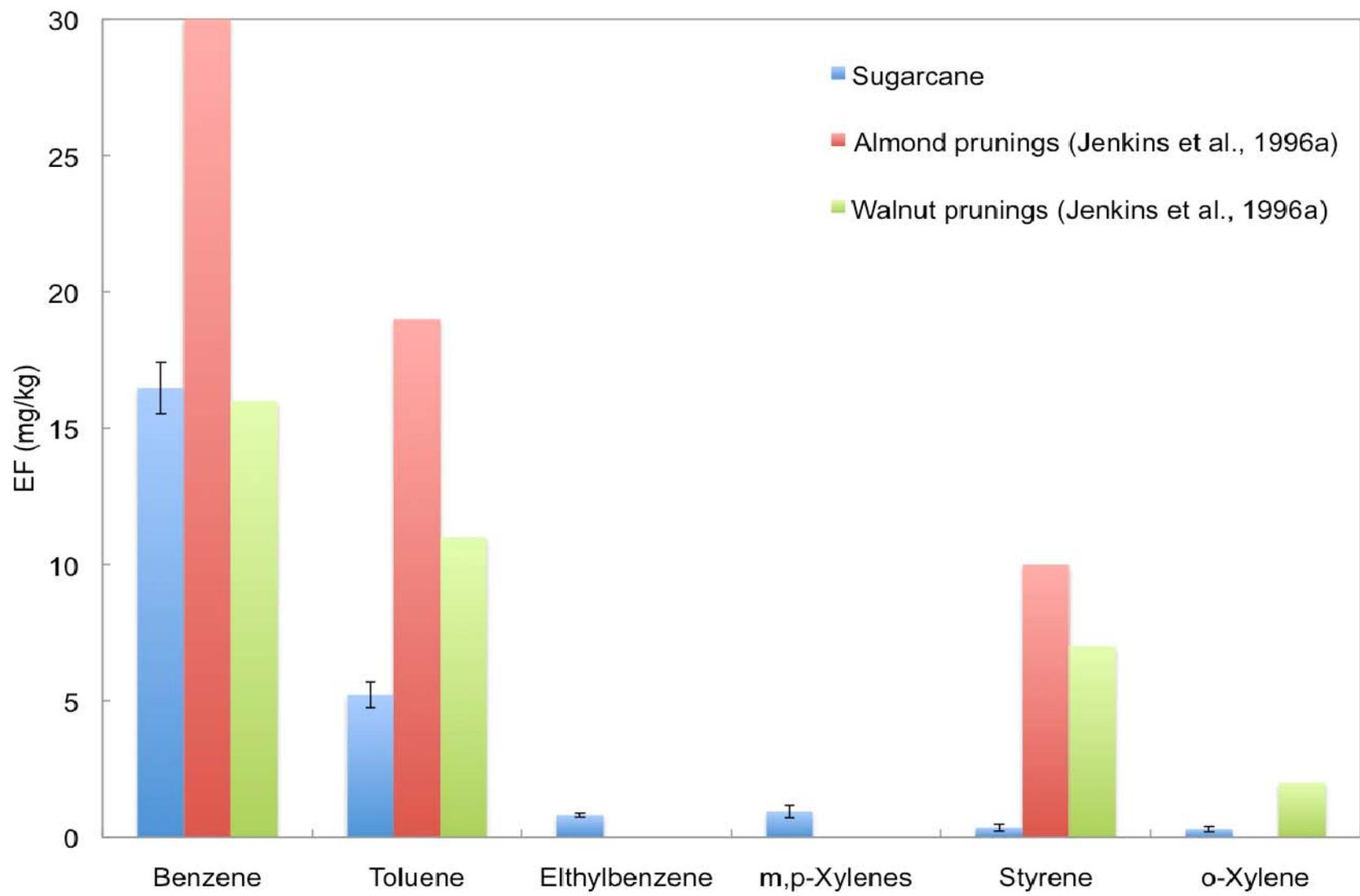


Figure 4-8. Comparison of VOC EF

CHAPTER 5 SUMMARY AND CONCLUSIONS

This study further 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}, OC and EC in a combustion chamber. In addition to quantifying EFs, specific compound patterns were identified, which can help in source apportionment studies and emission estimates.

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. 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 higher moisture content biomass (i.e., whole stalks) exhibited higher EFs. Also, more intense fires (characterized by higher fuel loading and temperatures) produced lower EFs.

It should be emphasized that field burning is characterized by numerous burning phases (i.e., smoldering, flaming) and is influenced by a number of variables (meteorological conditions, plant conditions, plant treatment, ect.). EFs are expected to be highly variable during the field burning process as well as highly variable during the harvesting period—as the meteorological and plant conditions will 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 (Jenkins et al., 1996b).

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 to evaluate the contribution of this source to local and state pollutant inventories. In addition, these data can be used in the National-Scale Air Toxics Assessment (NATA) to help identify important air toxic exposure sources with the goal of protecting public health. With more reliable data, regulatory agencies are able to more accurately model human and environmental exposure and to subsequently make better management and permitting decisions.

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BIOGRAPHICAL SKETCH

Danielle Lyon Hall was born in Silver Spring, Maryland in the summer of 1986. She graduated from Sarasota High School in 2004 and entered the University of Florida to study Environmental Engineering. As an undergraduate student she was very involved with her sorority, Kappa Alpha Theta, which she served as Vice-President of Finance and President in 2006 and 2007, respectively. She was also active in the American Water Works Association (AWWA), serving as treasurer, and in the Air & Waste Management Association (AWMA). Danielle began research as an undergraduate student, participating in the University Scholars Program under the direction of Dr. Chang-Yu Wu. She graduated summa cum laude with a B.S. in Environmental Engineering Sciences in December 2008.

Danielle began graduate school in January 2009 to focus on air quality research under the direction of Dr. Chang-Yu Wu. She continued to be active in professional organizations serving as president of AWMA and vice-president of AWWA during the 2008-2009 academic year. She graduated in May 2010 with a M.E. in environmental engineering sciences from the University of Florida.