EVALUATING EMISSION FACTORS OF PM$_{2.5}$, SELECTED PAHS AND PHENOLS FROM WHEAT AND KENTUCKY BLUEGRASS STUBBLE BURNING IN EASTERN WASHINGTON AND NORTHERN IDAHO

By

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To the Faculty of Washington State University:

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Abstract

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In 2002, over 100,000 acres of wheat and 40,000 acres of KBG stubble were burned in 18 counties of eastern Washington (WA) and northern Idaho (ID), on less than a tenth of the days of the year. Emission factors (EFs) of pollutants from post-harvest agricultural burning are required to predict downwind impacts of smoke, to assess control strategies and to inventory emissions. EFs of several pollutants from wheat and Kentucky bluegrass (KBG) stubble burning were evaluated during laboratory scale burn experiments conducted in a US EPA test burn facility. The EFs from wheat stubble burning were: PM$_{2.5}$: 3.0 ± 0.6 g kg^{-1}; levoglucosan (LG): 150 ± 130 mg kg^{-1}; particulate elemental carbon (EC): 0.35 ± 0.16 g kg^{-1}; artifact corrected particulate organic carbon (OC): 1.9 ± 1.1 g kg^{-1}; CO: 53 ± 8.0 g kg^{-1}; total hydrocarbons (THC): 2.2 ± 0.39 g kg^{-1}; sum of 19 solid+ vapor phase polycyclic aromatic hydrocarbons (PAHs): 17 ± 8.2 mg kg^{-1}; sum of 19 solid+ vapor phase methoxyphenols (MPs): 79 ± 36 mg kg^{-1}. Combustion

efficiencies (CE) of wheat burns ranged from 89–99%. For KBG, (CE range 82-96%) the EFs were: $PM_{2.5}$: 12±1.4 g kg^{-1}; LG: 350±510 mg kg^{-1}; EC: 0.63±0.056 g kg^{-1}; OC: 6.9±0.85g kg^{-1}; CO: 52±3.3 g kg^{-1}; THC: 11±1.3 g kg^{-1}; PAHs: 21±15 mg kg^{-1} and MPs: 35±24 mg kg^{-1}. $PM_{2.5}$, CO, THC, PAH, LG, OC and EC EFs from wheat are comparable to other similar studies reported in literature, but it is difficult to compare the KBG EFs due to the scarcity of published data. MP EFs appear more dependent on the stubble type, and are possibly linked to the lignin content therein. Using EFs found in this study, wheat and KBG burning was estimated to have produced between 0.04- 34.5% of $PM_{2.5}$ and CO emissions within the respective WA and ID counties, during 2002.

In general, when CE differences were taken into account, a reasonable degree of agreement was observed between EFs measured during field experiments, and those evaluated in the chamber. Ground based CO and CH_4 measurements showed similar EF-CE relationships with samples collected on board a light aircraft. This highlights the need for evaluating CEs along with EFs, to facilitate proper interpretation.

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DEDICATION

This dissertation is dedicated to my Lord and savior, Jesus Christ.

"Until my trophies at last I lay down…"

ATTRIBUTION

This dissertation comprises seven chapters. For each chapter, I was the primary author and was responsible for the organization and execution of experimental work, laboratory analyses and data processing described therein.

Chapter 1 lays out the overview and objectives of the research, and presents the organization of the following chapters. The reasons behind post- harvest agricultural burning, some important pollutants contained in smoke, the need for emission factors, and experimental methods used for determining them, are presented.

Chapters 2, 3 and 4 consist of individual manuscripts detailing specific aspects of the research, each formatted for submission to a peer reviewed scientific journal. Chapter 2 deals with emissions of fine particles, carbon monoxide and hydrocarbons from simulated agricultural burns. The work described in this chapter was conducted at the US EPA test burn facility, at the kind invitation of Dr. Brian Gullett of the EPA National Risk Management Research Laboratory. Dr. Abderrahmane Touati and Mr. Steve Terll, both of Arcadis Geraghty and Miller, worked tirelessly during the burn experiments. Mr. Eugene Allwine (WSU) helped design the tracer experiment and analyze the SF_6 samples.

Chapter 3 discusses emissions of polycyclic aromatic hydrocarbons, methoxyphenols, levoglucosan, elemental and organic carbon from the same burns. Research presented in this chapter was also conducted at the EPA test burn facility. Dr. Christopher Simpson (University of Washington, Seattle, WA) and Dr. Jeffrey Corkill (Eastern Washington University, Cheney, WA) kindly made available their GC- MS facilities for running PAH and MP analyses. Dr. Jorge Jimenez (WSU) conducted

levoglucosan analyses. Ms. Paige Witherington (Clemson University, SC), Ms. Karen Hirakawa (Whittier College, CA) and Ms. Melissa Zgola (Cornell University, NY) rendered valuable assistance in the field and laboratory.

Chapter 4 focuses on how well simulated burns represent field burns, by comparing the aforesaid pollutants emitted during each type of burn experiment. Mr. Shawn Nolph (Department of Ecology, WA) and Ms. Julie Simpson (Nez Perce Tribe, ID) coordinated the field burns. Several growers from WA and ID kindly hosted research teams during field burns. Mr. Lee Bamesberger and Mr. Eugene Allwine (both of WSU) helped with the analysis of syringe samples. Mr. Kyle Heitkamp and Ms. Willow Foster (both of WSU) assisted with the aircraft experiment. Mr. Ron Bolton (WSU) analyzed straw and ash for carbon content.

Chapter 5 highlights the details of two methods used to evaluate a sampling artifact. Organic carbon measurements can be overestimated due to vapor condensation on quartz filters, but the artifact can be remedied by deploying two filters in tandem. This chapter discusses the magnitude of the artifact, and compares the performance of two different dual- filter configurations.

Chapter 6 discusses some research that could be carried out as an extension of the work presented here. An experimental design to study the effects of smoke aging is proposed, and the development of an ozone denuder (necessary to minimize the oxidation of PAHs during sampling) is discussed. The research described in this chapter benefited from the services of Ms Karen Hirakawa and suggestions made by Mr. Eugene Allwine.

Chapter 7 discusses how the findings of this research address the scientific questions posed at the outset, summarizes the findings and draws conclusions.

1   INTRODUCTION

Southeastern Washington State (WA) and north central Idaho (ID) –an area known as the Palouse – is a productive wheat growing region. The average yield of wheat (*Triticum aestivum L.*) in the Palouse is 540 - 670 g m^{-2} (80 to 100 bushels acre^{-1}), compared with 200 - 270 g m^{-2} (30 to 40 bushels acre^{-1}) in the U.S. Midwest (Scheinost et. al, 2001). Sixty five percent of the Kentucky bluegrass (*Poa pratensis L.*) produced in the USA is also produced in this region (Mazzola et al., 1997). KBG is used in turfs, golf courses, nurseries and lawns.

1.1.   REMOVAL OF POST- HARVEST RESIDUES

Post-harvest field burning is practiced on the Palouse as a means of clearing agricultural residues. Some of the reasons why growers resort to burning as opposed to alternatives such as baling, composting and landfilling are (US EPA, 2001a; US EPA, 2001b; ASI, 2003; Roberts and Corkill, 1998; Johnston et al., 1996, WA DOE, 2003):

- Fire releases nutrients into the soil, thereby reducing the need for agro-chemicals.

- Burning helps with pest and disease control while increasing or at least sustaining yield.

- Reducing the residues facilitates the use of cost effective direct seeding techniques, which require no tillage and therefore reduces the potential for soil erosion.

- Combustion is a quick and inexpensive method for clearing residue.

- Mechanical removal of residue (baling), plowing back into the field, composting, landfilling or resale of stubble for offsite uses such as animal feeds, compression into briquettes or use as a raw material in processes such as chipboard manufacture, are not always cost effective.

Burning may be allowed if the grower is able to demonstrate a need for the following (WA DOE, 2003, US EPA, 2001b):

- Surface sanitation to achieve pest control

- Combating unmanageable weed residue

- Eliminating pests harbored in surface residue

- Clearing residue on complex terrain where farm machinery cannot be operated

In addition, permission to burn crop residue is usually granted depending on existing air quality in the area, expected meteorology in the locality, the possibility of air stagnation and non-exceedence of National Ambient Air Quality Standards (ISDA, 2003). Winds and proximity of fires to smoke sensitive areas are also considered when determining the extent of burning allowed. These factors confine agricultural burning to a narrow time window following harvest.

In 2002, 121,115 acres of cereal grain fields (~ 90% wheat) were burned in WA (WA DOE, 2004). Most of these fields were situated in 10 counties east of the Cascades. Washington State does not allow the burning of KBG fields, although Idaho does. KBG is produced in 8 north central and northern ID counties, which include two Native American reservations. In 2002, 5,070 acres of wheat and 46,081 acres of KBG were burned in these areas of ID (ISDA, 2003). Smoke produced during burning can trigger complaints from citizens in downwind areas (Jimenez, 2002). Figure 1.1 shows the view in the vicinity of field burns.

Figure 1.1:   Agricultural field burning in (a) Washington (wheat) and (b) Idaho (KBG).

1.2.   POLLUTANTS OF INTEREST

Pollutants emitted during agricultural burns include, among others, CO_2, CO, hydrocarbons, particles smaller than 2.5µm in aerodynamic diameter ($PM_{2.5}$), and Semi Volatile Organic Compounds (SVOCs- present in solid and vapor phases). $PM_{2.5}$ is a known trigger of respiratory health complications (Roberts and Corkill, 1998; Mar et al., 2004a; Mar et al., 2004b, Slaughter et al., 2003). Among the SVOCs that are formed during the combustion of biomass are polycyclic aromatic hydrocarbons (PAHs) and phenols. Several PAHs are carcinogenic and are associated with mutagenicity (Seinfeld and Pandis, 1997; Roberts and Corkill, 1998; Ramdahl and Becher, 1982).

Several methoxylated phenols (MPs; also classified as SVOCs), particularly syringyl and guaiacyl species, are used as markers of lignin combustion (Simpson et al., 2005; Simoneit, 2002). Relative proportions of 2-methoxyphenols (guaiacols) and 2,6-dimethoxyphenols (syringols) in MP emissions provide some insight into the type of biomass being combusted (Simoneit, 2002). 1,6-anhydro-β-D-glucopyranose, commonly known as levoglucosan (LG), is often reported along with MP measurements, as it is considered a marker of cellulose pyrolysis, and predominates in the solid phase (Hays et al., 2002 and 2005; Schauer et al.,

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2001). Data on MP and LG emissions can be used to develop source profiles for receptor models, which are tools for assessing the contribution of biomass burning to pollution episodes (Simoneit, 2002).

Elemental carbon (EC) and organic carbon (OC) can account for over 50% of the $PM_{2.5}$ mass in areas impacted by smoke from biomass burning (Reid et al., 2005; Seinfeld and Pandis, 1997). EC and OC emissions are inventoried since EC is an important species in radiative forcing, and OC includes species (such as PAHs) with toxicological properties.

1.3.   EMISSION FACTORS

Emission factors (EF) – defined as the mass of pollutants emitted per unit mass of dry stubble consumed by fire- are needed as input to dispersion models. EFs are also needed to develop emission inventories and to evaluate the effectiveness of pollution control strategies. EFs are influenced by factors that affect the combustion efficiency (CE) of the fire (Ward et al., 1992; Ward and Hardy, 1991). These include the amount of available oxygen, combustion temperature, stubble moisture content, residence time of ventilation air, prevalent meteorological conditions, rate of flame spread, fire management techniques and turbulence. EFs are also affected by the stubble characteristics including fuel type and chemical makeup, residue mass per unit area (loading), stubble orientation and extent of compaction in the field (Ward et al., 1992; Radke et al., 1988; ASI, 2003; Darley et al., 1974).

Laboratory scale experiments conducted in test burn chambers are often used to evaluate EFs from biomass burning (Jenkins et al., 1996; Ortiz de Zarate, 2000; Ramdahl and Becher, 1982; Oros and Simoneit, 2001; Hays et al., 2002 and 2005; Kjällstrand et al., 2000, Kjällstrand and Petersson, 2001). Sampling smoke and monitoring variables such as

ventilation and stubble mass consumption rates, is easier during chamber burns than with field burns. Further, if the chamber is well mixed and approximates the behavior of a continuous stirred tank reactor, the smoke sampled therein is likely to be representative of the whole plume.

Some studies have determined pollutant EFs based on experiments conducted in the field (ASI, 2003 and 2004; Hurst et al., 1994; Ward et al., 1992; Carroll et al., 1977; Boubel et al., 1969). Unlike in burn chambers, several additional variables including local meteorology, terrain, cropping and burning practices, presence of green grass, fire temperature, intensity, spread and burn rate come into play during field burns. Several of these factors affect the CEs (ASI, 2003; Jenkins et al., 1996; Carroll et al., 1977), and as a result, impact the EFs. Therefore it is necessary to understand how well chamber experiments represent field burns.

Conducting field experiments poses some challenges however, such as dealing with shifting wind directions, sampler power requirements etc. Ground-based smoke samples could be weighted toward smoldering emissions on account of lower plume buoyancy (Hurst et al., 1994; Ward et al., 1992). Similarly airborne samples collected aloft (for example, on board a light aircraft) may be weighted toward the more buoyant flaming emissions.

1.4. RESEARCH HYPOTHESES

The research conducted here stems from the following hypotheses:

- CE is one of the main variables affecting EFs.
- Chamber burns are hypothesized to provide reasonable representations of field scenarios.

- Most laboratory scale trials reported in the literature appear to involve the combustion of randomly piled up stubble and sampling of emissions. However, given the dependency of EFs on CE, it is hypothesized that controlled burns in which biomass is randomly piled, would have combustion characteristics different from those of field burns, owing to differing degrees of contact between the fuel and available oxygen. Therefore field orientation of stubble must be reconstructed during laboratory-scale experiments, for simulations to be more representative of field burns.

1.5. OBJECTIVES OF RESEARCH

The purpose of the research forming the basis of this dissertation, is to:

- Evaluate EFs of CO, hydrocarbons, $PM_{2.5}$, EC, OC, LG, PAHs and MPs from wheat and KBG burning as a function of CE, with the aid of chamber- scale burn experiments. An independent method used to calculate EFs (for subsequent use in field experiments) needs to be validated during the chamber burns.

- Compare the EFs evaluated in the chamber with those determined from field studies. A secondary objective during field experiments is the comparison of EFs calculated from ground based field samples, against those collected on board a light aircraft.

1.5.1. Chamber burns: emission factors of $PM_{2.5}$, CO and hydrocarbons

Few studies list EFs of pollutants from KBG stubble burning (Boubel et al., 1969, ASI, 2004). EFs for wheat grown and burned according to the practices in eastern WA are scarce (ASI, 2003). Chapter 2 is devoted to quantifying $PM_{2.5}$, CO and hydrocarbon emissions from wheat and KBG stubble burning. Laboratory-scale, controlled burn experiments were employed for the purpose.

To mimic field scenarios during chamber burns, the stubble was oriented and loaded to correspond to the wheat fields of eastern WA and KBG fields of northern ID (Figure 1.2). This chapter also reports on the validation of an independent method used to calculate EFs (for subsequent use in field experiments).

Figure 1.2:   Orientation of stubble in the field and (inset) chamber. (a) Wheat and (b) KBG

The research presented in Chapter 2 was published in the journal *Atmospheric Environment*. Material that was excluded from the journal article due to space limitations, is presented in Appendix A.

1.5.2. Chamber burns: EFs of PAHs, MPs, LG, EC and OC

While PAH, MP and LG emissions from burning wood and forest debris are documented, a recent review paper (Lemieux et al., 2004) shows few studies reporting emissions of PAHs from agricultural burning. Additionally, two studies involving wheat and KBG burns (ASI, 2003 and 2004, respectively) in eastern WA and northern ID provide limited PAH data. A literature survey shows only one study (Hays et al., 2005) detailing the MP and LG emissions from agricultural burning, and part of the data in that study was collected during the experiments described in this dissertation.

Data on EC and OC emissions from agricultural burning are also scarce (Turn et al.,

1997; Hays et al., 2005). It is known that a sampling artifact caused by SVOC adsorption on quartz filters positively biases OC measurements (Kirchstetter et al., 2001; Subramanian et al., 2004; Turpin et al., 1991). However literature reporting OC EFs from biomass burns (e.g. Turn et al., 1997; Christian et al., 2003; Hays et al., 2005) does not mention an artifact correction, and as a result, the accuracy of OC EFs is unknown.

Chapter 3 reports on the determination of EFs of 19 PAHs (including all species on the former "priority PAH" list), 19 MPs (9 guaiacyl and 10 syringyl species, often reported in recent literature), LG, EC and artifact corrected OC from wheat and KBG stubble burning. Sampling was conducted during the experiments described in Chapter 2.

The research presented in Chapter 3 was submitted for publication in the journal *Atmospheric Environment*. Material that was excluded from the journal article due to space limitations, is presented in Appendix A.

1.5.3. Field burns: comparison with chamber burns

Data from the above-mentioned chamber experiments cannot be readily compared against field data in literature, since few field studies have been conducted to determine EFs from wheat and KBG burning (Darley et al., 1974; Boubel et al., 1969; A.S.I. 2003 and 2004). These few studies focus mostly on particulate matter, CO and hydrocarbon emissions, and the A.S.I studies provide very limited data on solid phase PAH emissions. We are unaware of field studies reporting EFs of EC, OC, MPs (solid or vapor phase) and vapor phase PAHs, from wheat and KBG burns.

Chapter 4 describes the comparison of CE-EF relationships for $PM_{2.5}$, CO, EC, OC, MPs and PAHs from wheat field burns (conducted in eastern WA) and KBG field burns (conducted in northern ID), with the corresponding measurements made in the burn

chamber. Further, EFs calculated from ground based field samples are compared against those collected on board a light aircraft.

The research presented in Chapter 4 was submitted for publication in the journal *Atmospheric Environment*. Material that was excluded from the journal article due to space limitations, is presented in Appendix B.

1.5.4. Measurement of OC adsorption artifact

The extent of SVOC adsorption on to quartz filters (positive artifact) is usually evaluated with one of two methods (Mader et al., 2003; Pang et al., 2002; Turpin et al., 1994; Eatough et al., 1993):

1. Deploying a quartz filter deployed downstream of the main quartz filter (QbQ)

2. Deploying a quartz filter downstream of a separate Teflon filter (QbT)

Chapter 5 discusses the assumptions of the QbQ and QbT methods, presents data on the magnitude of the artifact, and compares the QbQ and QbT methods.

1.5.5. Extension of research

Secondary OC can be formed as plumes are transported downwind (Turpin et al., 1991). Solid phase PAH- O_3 reactions and vapor phase PAH- OH radical reactions can both result in PAH lifetimes of less than an hour (rate constants from Pöschl et al., 2001; Alebić-Juretić et al., 1990; Calvert et al., 2002). MPs have been reported to react with PAHs (Kjällstrand and Petersson, 2001; McDow et al., 1994). Therefore solid+ vapor phase EFs of organic species presented in chapters 2-4 are valid at the point of emission only.

Secondary atmospheric transformations that are important over time scales of several hours must be accounted for in order to accurately predict downwind impacts of smoke from agricultural burning. Chapter 6 contains some ideas for experiments to study the effects of

smoke aging. Ozone formation occurs in aged smoke plumes and O_3 has been shown to oxidize solid phase PAHs (Pöschl et al., 2001; Alebić- Juretić et al., 1990; Finlayson-Pitts and Pitts, 2000) leading to underestimation of PAHs. The development and testing of a denuder (for removing O_3 from the gas stream, thereby minimizing the potential for PAH degradation during sampling) is also discussed.

1.5.6. Conclusions

Chapter 7 draws conclusions from the work presented in preceding chapters, and discusses how well the original scientific objectives of the research have been addressed. Emission factors weighted by phase of combustion, are evaluated for use in subsequent modeling work.

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2   PARTICULATE EMISSIONS FROM WHEAT AND KENTUCKY BLUEGRASS STUBBLE BURNING IN EASTERN WASHINGTON AND NORTHERN IDAHO

Particulate emissions from wheat and Kentucky bluegrass stubble burning in eastern Washington and northern Idaho

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2.1. ABSTRACT

The $PM_{2.5}$ emission factors (EF) in smoke from post- harvest wheat and Kentucky Bluegrass (KBG) stubble burning were quantified in the United States Environmental Protection Agency test burn facility. The $PM_{2.5}$ EFs from high and low combustion efficiency (CE) wheat burns were 0.8 ± 0.4 g kg^{-1} and 4.7 ± 0.4 g kg^{-1} respectively, and decreased with increasing CE. While these EFs are generally in agreement with literature, it is difficult to compare the $PM_{2.5}$ EFs from KBG burns (12.1 ± 1.4 g kg^{-1}) due to the scarcity of published data. Wheat burns conducted with randomly piled stubble resulted in $PM_{2.5}$ EFs different to those where the stubble was oriented as found in the field post harvest. Two separate methods for estimating EFs were employed and found to be in good agreement. The carbon in the biomass was almost quantitatively accounted for by measuring CO_2, CO, total hydrocarbons (THC) and $PM_{2.5}$ emissions. The $PM_{2.5}$/ CO emission ratios for wheat (0.05 ± 0.01) agree with literature data, while the same ratio for KBG (0.23 ± 0.02) was

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slightly higher than data reported. These ratios exhibit low dependence on CE and can be used to predict the level of one pollutant in a plume, when the concentration of the other is known. Wheat and KBG fields in 18 counties of eastern Washington and northern Idaho are burned on less than a tenth of the days of the year. Yet the fires were estimated to have produced between 0.04- 34.5% of the total $PM_{2.5}$ and CO emissions within the respective counties, during 2002.

Keywords: $PM_{2.5}$, emission factor, combustion efficiency, carbon mass balance, emission ratio

2.2. INTRODUCTION

Southeastern Washington (WA) and north central Idaho (ID) are among the most productive wheat growing regions in the world (Scheinost et. al, 2001). In addition 65% of the Kentucky bluegrass (*Poa pratensis* L., KBG) produced in the USA was also produced in this region (Mazzola et al., 1997). KBG is still produced in northern ID and on a smaller scale in eastern WA. Post-harvest field burning is commonly practiced for clearing agricultural residues. Growers resort to burning rather than its alternatives (baling, composting, land filling, crop rotation, compression into briquettes and use as a raw material in processes such as chipboard manufacture) for the purposes of pest and disease control, increased yield, tillage reduction (lower potential for soil erosion), reduction of agrochemical usage, convenience and cost effectiveness (US EPA, 2001a; US EPA, 2001b; ASI, 2003; WA DOE, 2003; Roberts and Corkill, 1998; Johnston et al., 1996).

Pollutants emitted from agricultural fires include, among others, CO_2, CO, hydrocarbons, and particulate matter nominally smaller than 2.5μm in aerodynamic diameter ($PM_{2.5}$). $PM_{2.5}$ is a known trigger of respiratory health complications (Roberts and Corkill,

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1998; Mar et al., 2004a; Mar et al., 2004b, Slaughter et al., 2003). Knowledge of emission factors (EF) – defined as the mass of pollutants emitted per unit mass of dry stubble burned- is needed as input to dispersion models that serve as management tools. EFs are also needed in emission inventories and to evaluate the effectiveness of pollution control strategies.

EFs are influenced by factors that affect the combustion efficiency (CE) of the fire (Ward et al., 1992; Ward and Hardy, 1991). These include the amount of available oxygen, combustion temperature, stubble moisture content, residence time of ventilation air, prevalent meteorological conditions, rate of flame spread, fire management techniques and turbulence. EFs are also affected by the stubble characteristics including fuel type and chemical makeup, residue mass per unit area (loading), stubble orientation and extent of compaction in the field (Ward et al., 1992; Radke et al., 1988; ASI, 2003; Darley et al., 1974).

Few studies list EFs of pollutants from KBG stubble burning (Boubel et al., 1969, ASI, 2004). Region specific EFs for wheat are scarce (ASI, 2003). The United States Environmental Protection Agency (US EPA) AP-42 (US EPA, 1995) provides EFs of total suspended particulate matter, CO and hydrocarbons from burning wheat and grasses. Both wheat and grass EFs are based on a single study (Darley et al., 1974 and Boubel et al., 1969 respectively) in which stubble orientation in the field has not been reconstructed during laboratory experiments. The Darley et al. study evaluates EFs according to the EF(carbon) method (see section on Alternative method for calculation of EFs), but neglects the contribution of CO, total hydrocarbons (THC) and $PM_{2.5}$ to the carbon mass balance (~10% error). The Boubel et al. study involves only 4 KBG burns at 5% and 23% stubble moisture. The data therein show a decrease in particulate, CO and hydrocarbon EFs with increasing

fuel moisture, whereas the opposite trend is expected (ASI, 2003, Carroll et al., 1977, Darley et al., 1974).

The objectives of the research reported here are to quantify $PM_{2.5}$ emission factors from the combustion of wheat and KBG stubble collected in eastern WA and northern ID, and validate one of the methods used to calculate EFs (see section on Alternative method for calculation of EFs). Since field experiments are not easily conducted or replicated, we simulated the field burns with laboratory-scale, controlled burn experiments. Field scenarios were mimicked during the laboratory burns, by reproducing the field orientation and loading of the stubble.

2.3. MATERIALS AND METHODS

The wheat stubble tested was irrigated winter wheat straw (*Triticum aestivum* L., variety Madsen). The stubble moisture content in wheat and KBG was measured immediately after obtaining the stubble from the field (see Table 2.1), and had not changed by more than 2% by the time burns were conducted.

Burn experiments were conducted at the US EPA open burn test chamber in Research Triangle Park, NC, in May 2001, August 2001 and August 2003. The burn chamber is described in detail by Lemieux et al. (2000). Between August 2001 and August 2003, the chamber was re-built in another location, though the same air supply fans and ducts were used in the new chamber. The internal volumes of both chambers were approximately 20 m^3. The chambers were operated in a flow-through manner and assumed to be well mixed.

In the middle of the burn chamber was a weighing platform, on which 725- 800g stubble was mounted to correspond to the orientation and loading in the field post harvest.

Stubble was ignited manually with a propane torch and the chamber door was closed immediately. The flaming phase typically lasted 1-2 minutes, followed by about 15 minutes of smoldering. As the instantaneous O_2 concentrations were always $\geq 18.5\%$ (v/v), the O_2 supply was deemed sufficient for combustion. The ash remaining accounted for $3.6\pm0.1\%$ (n= 91) of the mass of dry stubble exposed to the fire.

5 burns involving randomly piled wheat stubble were conducted in May 2001, to assess the effect of stubble orientation on EFs. A lower volumetric flowrate of chamber air was employed in August 2001, which raised the incremental chamber temperatures (ΔT: average temperature during sampling period minus pre-burn chamber temperature) due to lowered dilution rates. CEs and stubble consumption rates were also lower during August 2001, compared to May 2001.

2.3.1. Sampling and analysis

$PM_{2.5}$ mass measurements were made with the use of integrated low-volume (5 L min^{-1}) air samplers (Airmetrics Inc.), fitted with a $PM_{2.5}$ size selective inlet. Teflon filters were loaded on to lo-vol samplers for capturing particles for later gravimetric analysis. Quartz filters were used in some lo-vol samplers for Total Carbon (TC) analyses (not reported in detail here). Prior to and after sampling, Teflon filters were equilibrated in a controlled chamber (RH 45-55%, T 22- 26ºC) for 24 hours and weighed with a Cahn C-34 microbalance (Cahn Instruments, CA, USA). The reproducibility of replicate $PM_{2.5}$ measurements was 3.9% (based on n=39 during August 2003 experiments).

Continuous $PM_{2.5}$ monitoring was conducted using a DataRAM 2000 (MIE, Inc.) nephelometer, which was calibrated against the lo- vol samplers. Gaseous pollutants measured continuously included CO [Horiba VIA 510, dual beam Non-Dispersive Infra Red

(NDIR)], CO_2 (Rosemount 880A, NDIR), O_2 (Rosemount 755, paramagnetic susceptibility) and THC (TECO THC 51, Flame Ionization Detector. These detectors respond poorly to oxygenated non- methane hydrocarbons, but this uncertainty affects the calculations by <5%). The continuous gas analyzers were operated in accordance with the procedures outlined in 40 CFR Part 60, Appendix A, Method 6C. Pollutant samplers were placed close to the stack exit. Stubble mass loss and chamber temperature were also monitored continuously. Sampling was carried out for about 20 minutes, from the time of ignition.

Burn- specific background concentrations of CO_2, CO, THC and $PM_{2.5}$ (i.e. pre-ignition concentrations recorded by the continuous monitors) were assumed to remain constant over the sampling period. Pertinent experimental details are summarized in Table 2.1.

2.3.2. Calculation of Emission Factors

If a steady-state flow-through chamber is well mixed, uniform conditions and concentrations are expected throughout the chamber and will equal those in the exit stream (Cooper and Alley, 1994). The EFs were thus determined as follows:

$$EF_x \text{ (g kg}^{-1}) = (\Delta C_x \times Q_{chamber} \times t_{run}) / (1000 \text{ mg g}^{-1} \times m_{burned}) \qquad (1)$$

Where EF_x = Emission factor in g of pollutant X per kg dry stubble burned

ΔC_x = Exit concentration of pollutant X in excess of the background, mg m^{-3}

$Q_{chamber}$ = Flow rate of dilution air into the burn chamber, m^3 min^{-1}

t_{run} = Sampling time, min

m_{burned} = Mass of dry stubble consumed during the burn, kg

This method of calculating EFs is referred to as EF(direct) henceforth.

The degree of mixing in the chamber was assessed to justify the application of the well-mixed flow through model. Additional $PM_{2.5}$ samples obtained in an opposite corner of the chamber during the KBG burns, differed from the main sample by an average of 4.1% (n=11), although the difference is not significant ($t_{0.05,10} = 1.19$, P=0.26 for a paired t test). Neither is this difference significantly affected by the chamber air flowrate ($t_{0.05,4} = 0.71$, P=0.52).

Further, four thermocouples were placed around the chamber to assess if temperature was uniformly distributed. Two factor ANOVA was performed with a SAS program (SAS Institute Inc., Cary, NC, USA) and it was found that the temperatures did not vary significantly from one area of the chamber to another ($F_{3,115}= 0.33$, P=0.806). Neither did the air flowrate into the chamber have a significant effect on the temperature distribution throughout the chamber ($F_{1,115}= 1.85$, P=0.176). It was concluded that conditions throughout the chamber were uniform, and that the well-mixed flow through model reasonably described the burn chamber.

2.3.3. Measurement of chamber air flowrate

The flowrate of chamber air ($Q_{chamber}$) was initially measured by multiplying the linear velocity of air in the air supply duct to the chamber, by the duct cross sectional area. Velocity measurements were made upstream of the air supply fan using a pitot tube. However, since air leaks at the flanges of the fan were observed, a pair of SF_6 tracer experiments was conducted in July 2004 to better evaluate $Q_{chamber}$. Chamber air flowrates used during each of the previous campaigns were recreated by adjusting the fan speed, so as to obtain the previous linear velocities of air through the duct. SF_6 was introduced into the duct, downstream of the fan and the air leaks at the flanges were assumed to remain at a

constant fraction of the flow for all experiments. No air leaks were present downstream of the SF_6 release point.

At each fan speed setting, grab samples of air were drawn into 30 mL plastic syringes, at the chamber exit stack. Samples were analyzed for SF_6 on a gas chromatograph fitted with an electron capture detector (GC- ECD). SF_6 losses during transport and handling were negligible.

Chamber air flowrates were calculated to be 9.6 m^3 min^{-1} (May 2001 and first 11 burns of August 2003) and 14.0 m^3 min^{-1} for the last 19 burns of August 2003. For August 2001, $Q_{chamber}$ was estimated to be 7.2 m^3 min^{-1}, based on pitot tube data and the average leak rates determined from the SF_6 experiments. The relative standard deviation (RSD) of calculated flow rates did not exceed 2% but an error of 15% (twice the largest RSD of the pitot tube measurements) is assigned to the value of $Q_{chamber}$ to account for uncertainties with the estimation of leaks during the past burn experiments.

The tracer experiment was also used to determine if the exhaust from the chamber could be recirculated through the air intake, thereby biasing the background signal. During the burns, integrated SF_6 samples were drawn at the chamber air intake. Since SF_6 concentrations in these samples were below detection limits, it was concluded that no pollutants were recirculated.

2.3.4. Combustion Efficiency

The CE is defined as the fraction of the total carbon released in the form of CO_2 during combustion. The total carbon (C) released is calculated by the sum of the C concentrations in CO_2, CO, THC and $PM_{2.5}$ (Turn et al., 1997, Ward et al., 1992).

$$CE, \% = \frac{\Delta CO_{2-c}}{(\Delta CO_{2-c}) + (\Delta CO_{-c}) + (\Delta THC_{-c}) + (\Delta PM_{2.5-c})} \times 100 \qquad (2)$$

Where ΔCO_2-C (mg m^{-3}) = [mass fraction of C (w/w) in CO_2 (i.e. 12/44)] × [background-corrected average CO_2 concentration in burn chamber (mg m^{-3})]

$\Delta CO-C$ (mg m^{-3}) = 12/28 × [background-corrected CO concentration (mg m^{-3})]

$\Delta THC-C$ (mg m^{-3}) = [background-corrected THC concentration (mg m^{-3})]. CH_4 was used as the calibrant and the analyzer reports ppm C. [However THC EFs were calculated assuming the average composition of C_3H_8 (Nelson, 1982)].

$\Delta PM_{2.5}-C$ (mg m^{-3})= C content of $PM_{2.5}$ × [background-corrected $PM_{2.5}$ concentration (mg m^{-3})]. TC analyses, when corrected for adsorption artifacts (Turpin et al., 1994), show that the C content of $PM_{2.5}$ is 62.5% for wheat and 63% for KBG. This is similar to results reported by Crutzen and Andreae (1990) (66%), Ward et al. (1992) (62.5%) and Cachier et al. (1995) (73%), although it is unclear whether those authors accounted for the above-mentioned artifact.

2.3.5. Alternative method for calculation of EFs

This method, hereafter referred to as EF(carbon), is based on the conservation of C in the biomass, and does not require pre-and post-burn weighing of biomass (ASI, 2003, Andreae and Merlet, 2001). The EF(carbon) method is used for evaluating EFs during field experiments (Hurst et al., 1994; Ward et al., 1992; ASI, 2003; Andreae and Merlet, 2001) and is used here for validation purposes and comparing against the EF(direct) method.

$$EF_x \text{ (g kg}^{-1}) = \frac{\Delta C_x \times (1,000 \text{ g kg}^{-1}) \times C_{fraction}}{(\Delta CO_{2-C} + \Delta CO_{-C} + \Delta THC_{-C} + \Delta PM_{2.5-C})} \qquad (3)$$

Where $C_{fraction}$ is the mass fraction of C in dry stubble. In May and August 2001 the $C_{fraction}$ of wheat was 0.434 and 0.442, respectively (calculated from data in Gullett and Touati, 2003). The $C_{fraction}$ of KBG in August 2003 was measured (CNS2000 total carbon

analyzer, LECO Corporation, St. Joseph, MI) as 0.451±0.003 (n=4, ~ 0.3g sample per analysis). These data agree with Jenkins et al. (1996) ($C_{fraction}$ 0.443) and Ortiz de Zarate et al. (2000) ($C_{fraction}$ 0.44±0.016).

The assumptions made in the EF(carbon) method are:

1. Physico-chemical processes between emission and sampling are considered to have negligible effect on the pollutant concentrations. This constraint is reasonably well satisfied since samplers were placed a few meters away from the source. All pollutants are present in a unit volume of air sampled, in the same proportion in which they were produced by the fire (Nelson, 1982; Radke et al., 1988).

2. The C release rate is proportional to the mass loss rate of the fuel (Susott et al., 1991).

3. Stubble and ash have similar $C_{fractions}$ (Nelson, 1982; ASI, 2003). We found the $C_{fraction}$ in KBG ash to be 0.453±0.011 (n=4), which is very close to that of unburned stubble. Moreover these $C_{fractions}$ are assumed to be representative of the whole field.

4. All C in the biomass consumed by the fire is released into the atmosphere during combustion, and can be accounted for by measuring concentrations of CO_2, CO, THC and $PM_{2.5}$ in the plume (Radke et al., 1988; Andreae and Merlet, 2001). Time averaged concentrations of these pollutants are considered to be representative of the entire plume over the whole sampling period (Nelson, 1982), if the sampling period extends over the total burning time. A carbon mass balance closure is used [Equation (4)] to validate this assumption.

$$\text{Biomass C accounted for,}\% = \frac{\left(\Delta CO_{2-C} + \Delta CO_{-C} + \Delta THC_{-C} + \Delta PM_{2.5-C}\right)}{m_{burned} \times C_{fraction} \times 0.01} \times Q_{chamber} \times t_{run} \quad (4)$$

In May 2001, August 2001 and August 2003, 106.5±4.6%, 111.2±4.4% and 93.1±6.8% of biomass C, respectively, was accounted for by measuring these 4 species. The

few reported carbon mass balances [Nelson (1982): 91.8-114.3%; Hurst et al. (1994): 95±4.3%; Boubel et al. (1969): 99±10%] are in agreement. Therefore assumption #4 was deemed reasonable.

Unless otherwise stated, all EFs reported here are calculated with the EF(direct) method. All data were checked for normal distribution and uncertainties associated with results follow the format "mean±95% confidence interval". Based on propagation of error analysis, the EF(direct) and EF(carbon) have uncertainties of ±20%.

2.4. RESULTS AND DISCUSSION

As seen in Figures 2.1-2.3, EFs of $PM_{2.5}$, CO and THC show inverse relationships with CE. The EFs of $PM_{2.5}$ (Figure 2.1) and THC (Figure 2.3) from KBG burns are higher than in wheat burns, although the CO EFs are comparable (Figure 2.2). The lower CE KBG burns are also characterized by slower stubble consumption rates and significantly lower ΔTs than wheat burns ($t_{0.05,35}$=5.2, P<0.001, comparing burns with the same m_{burned} and $Q_{chamber}$).

CE variations explain 60% or more of the $PM_{2.5}$, CO and THC fluctuations (Figure 2.2). The bulk of C is emitted as CO_2: 94.5 and 90.4% on average for wheat and grass stubble, respectively. Table 2.2 shows how emission factors measured in this study compare with those found in literature. The May 2001 wheat burns may have been operated at CEs slightly higher than those typically seen in the field. Nevertheless overall averages of EFs from wheat straw burning are in reasonable agreement with published values, including those involving some other stubble types.

EFs from KBG are difficult to compare against those reported by Boubel et al. (1969), due to the few data points (n=4) and unexpected stubble moisture-EF relationship in

that study. Though $PM_{2.5}$ and CO EFs are lower than those in ASI (2004), the ASI (2004) field study was characterized by (i) CEs lower than those we encountered, partly due to higher stubble moisture content (ii) high RSD of $PM_{2.5}$ EFs and (iii) a weak $PM_{2.5}$ EF- CE correlation ($R^2 = 0.22$).

The average combustion efficiencies of the burns performed in May 2001 on randomly piled wheat stubble were 1% lower than the corresponding CE's of the oriented burns. $PM_{2.5}$ EFs of oriented burns (range 0.1- 2.5, average 0.5) were lower than randomly piled burns (range 0.6- 4.1, average 1.9). A larger burn-to-burn variation is associated with the random stubble orientation. While more tests at CEs typical of field burns are required in this regard, the data available here suggest that fuel orientation does affect the EFs.

The magnitude of the differences between EF(direct) and EF(carbon) are the same for CO_2, CO, THC and $PM_{2.5}$ emitted during a particular burn. EF(carbon) expressed as a % of EF(direct) was 94.4±4.2% (May 2001), 91.1±3.9% (August 2001) and 110.7±7.2% (August 2003). Since the differences are within experimental error, the two methods for estimating EFs compare well. If all C in the stubble was converted to CO_2 (i.e. CE 100%) the CO_2 EF is given by ($C_{fraction} \times 1000 \times 44/12$) g kg^{-1}. Table 2.3 shows that the CO_2 EFs are consistent with these upper limits when the confidence intervals are considered.

Emission Ratios (ER) can be computed for pollutants that are emitted during the same phase of combustion, and exhibit low dependence on CE (Andreae and Merlet, 2001; Ortiz de Zarate et al., 2000; Hurst et al., 1994; Ward et al., 1992). ERs can help predict the level of one pollutant in a plume, when the concentration of the other is known. The average $PM_{2.5}$/ CO ER for wheat is in agreement with data in literature (Table 2.2), while bluegrass

fires have higher $PM_{2.5}$/ CO ratios than wheat. The KBG ER is slightly higher than those by ASI (2004) and Boubel et al. (1969).

2.4.1. Annual emissions from wheat and KBG stubble burning

In WA, cereal stubble burning (90% wheat) occurs in 10 counties east of the Cascades. Typically no KBG is burned in WA. Turf grasses (90% KBG) are produced in 8 north central and northern ID counties, which include two Native American reservations. These 18 WA and ID counties are located in common or adjacent airsheds. For 2002, the total $PM_{2.5}$ and CO emissions from wheat and KBG burning in this area were evaluated as: Area burned (m^2) × Residue loading in field (kg m^{-2}) × Dry Matter Content of Residue (%) × Burning Efficiency (i.e. % dry biomass consumed by fire) × Pollutant EF (g kg^{-1}).

We estimate the emissions from wheat burning in the airshed(s) to be 0.7 Gg $PM_{2.5}$ and 12.3 Gg CO. Similarly KBG burning released 0.6 Gg $PM_{2.5}$ and 2.5 Gg CO, during 2002. Data sources are: acreage burned and loading- WA DOE (2004) and ISDA (2003); wheat and KBG fractions among cereals and turf grasses grown- USDA (2002); loadings and burning efficiencies- ASI (2003 and 2004); dry matter content- Table 2.1; EFs: Table 2.2.

Total $PM_{2.5}$ and CO emissions from wheat and KBG burning in 2002 were compared against $PM_{2.5}$ and CO emissions from mobile, stationary, point and area sources, inventoried in these counties (WA DOE, 2004; IDEQ, 2005). Wheat burning in the 10 WA counties accounted for 3.7% of annual $PM_{2.5}$ emissions (range 0.04- 18.5%) while CO emissions made up 7.7% (range 0.1- 34.5%). CO inventories from 4 ID counties were available for comparison. KBG and wheat burning therein accounted for 2.2% (range 1.1- 4.3%) of annual CO emissions. Though these appear to be relatively small fractions, it must be borne

in mind that agricultural burning only occurs during a few weeks each year (33 and 23 days in 2002, in WA and ID respectively). Thus short- term contributions from agricultural burning to the local emissions can be substantial.

2.5. CONCLUSIONS

EFs are smoke management tools; dispersion models employed within forecast systems (such as the ClearSky project -http://www.clearsky.wsu.edu) could utilize region-specific EFs and assist authorities determine the advisability of agricultural burning. Knowledge of KBG EFs is scarce and would benefit the smoke managers in areas where KBG stubble is burned. On average, the EFs of $PM_{2.5}$, CO and THC were 3.0±0.6, 52.9±8.0 and 2.2±0.4 g kg^{-1}, respectively for wheat stubble, and 12.1±1.4, 51.8±3.3 and 10.7±1.3 g kg^{-1}, respectively for KBG. Since EFs of these pollutants are inversely correlated with CE, identifying methods of increasing the CEs of burns would help reduce the emissions from agricultural field burning.

The assumptions made in the EF(carbon) method are reasonable, and it is a viable tool for use during field experiments. An example of the application of ERs would be the estimation of $PM_{2.5}$ concentrations in a plume, by measuring CO. Sampling $PM_{2.5}$ on board an aircraft requires a specially designed isokinetic sampling inlet. But CO could be measured more easily and multiplied by a previously determined ER, to estimate the $PM_{2.5}$ level.

Randomly piled stubble could represent varying degrees of stubble compaction, which appears to influence $PM_{2.5}$ EFs. The compact-ness of KBG straw implies less contact with ambient air compared to the more spaced out, hollow, wheat straw. Compared to wheat, a larger KBG stubble mass fraction was consumed during the slow propagating, low

CE smoldering phase, which also dissipates less heat than flaming combustion. These factors could partly explain the observed differences between CEs, ΔTs and burn rates of wheat and KBG fires.

2.6. ACKNOWLEDGEMENTS

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2.8. LIST OF FIGURES

Figures 2.1-2.3: Plots of $PM_{2.5}$, CO and THC emission factors vs. combustion

efficiency.

Table 2.1:   Summary of experiments conducted and samples collected

Parameter measured	Wheat Stubble		Grass
	May 2001	August 2001	August 2003
% H_2O at burn time (w/w wet basis)	8.9	8.8	9.0
No. of burns/ Valid $PM_{2.5}$ samples on Teflon filters/ DataRAM $PM_{2.5}$	30/ 28/ 27	31/ 31/ 23	30/ 85/ 30
Valid O_2, CO_2, CO and THC data, temperature and stubble mass	THC for 25 burns, rest 30	Data for 31 burns	Data for 30 burns

Table 2.2:   Emission factors (g kg^{-1}) and emission ratios from biomass burning. Based on burns for which all pollutants were available.

| | KBG (CE 90.4±1.0%, n=30) | Wheat stubble | | | Literature |
		May 2001 (CE 97.7± 0.3%, n=23)	Aug 2001 (CE 92.2± 0.5%, n=31)	Overall average (CE 94.5± 0.8%, n= 54)	
PM$_{2.5}$	12.1±1.4	0.8±0.4	4.7±0.4	3.0±0.6	4.2[a], 3.6±0.7[b], 3[c], 6.2[d], 5.6[e], 29.6±10.4[f], 8[g], 8.5[h]
CO	51.8±3.3	21.1±1.9	76.5±5.1	52.9±8.0	38.2[a], 44.1±7.4[b], 86[d], 190±38[f], 61[g], 59[h], 80[i], 35[j],
THC	10.7±1.3	1.1±0.4	3.0±0.5	2.2±0.4	2.9[a], 8.7[g] (as C$_3$H$_8$), 7[i],
PM$_{2.5}$/ CO ER	0.23±0.02	0.03±0.01	0.06±0.01	0.05±0.01	0.08±0.01[b], 0.06[d], 0.17±0.05[f], 0.14[g], 0.07[j]

References used in Table 2.2

a. Dennis et al. (2002); wheat fires
b. ASI (2003); wheat (CE 95.6±0.8%)
c. USFS CONSUME Model, forest fires
d. Ward et al. (1992), forest fires
e. From data in Turn et al. (1997), wheat
f. ASI (2004), KBG (CE 84.5±3.1%)
g. Boubel et al. (1969), KBG (CE 90%)
h. EPA AP-42 (1995). Head + back fires, wheat
i. Hurst et al. (1994), savannah fires
j. Ortiz de Zarate et al (2000), wheat

Table 2.3: CO_2 EF consistency check. Based on burns for which all pollutants were

available.

	Upper limit, based on C in biomass, g kg^{-1}	Measured EF, g kg^{-1}
May 2001	1596	1658±72
August 2001	1620	1664±68
August 2003	1654	1403±117

3   EMISSION FACTORS OF PAHS, METHOXYPHENOLS, LEVOGLUCOSAN, ELEMENTAL CARBON AND ORGANIC CARBON FROM SIMULATED WHEAT AND KENTUCKY BLUEGRASS STUBBLE BURNS

Submitted to Atmospheric Environment

Emission factors of PAHs, methoxyphenols, levoglucosan, elemental carbon and organic carbon from simulated wheat and Kentucky bluegrass stubble burns

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3.1. ABSTRACT

Emission factors (EFs) of pollutants from post-harvest agricultural burning are required for predicting downwind impacts of smoke and inventorying emissions. EFs of polycyclic aromatic hydrocarbons (PAH), methoxyphenols (MP), levoglucosan (LG), elemental carbon (EC) and organic carbon (OC) from wheat and Kentucky bluegrass (KBG) stubble burning were quantified in a US EPA test burn facility. The PAH and MP EFs for combined solid + gas phases are 17 ± 8.2 mg kg^{-1} and 79 ± 36 mg kg^{-1}, respectively, for wheat and 21 ± 15 mg kg^{-1} and 35 ± 24 mg kg^{-1}, respectively, for KBG. LG, particulate EC and artifact-corrected OC EFs are 150 ± 130 mg kg^{-1}, 0.35 ± 0.16 g kg^{-1} and 1.9 ± 1.1 g kg^{-1}, respectively, for wheat and 350 ± 510 mg kg^{-1}, 0.63 ± 0.056 g kg^{-1} and 6.9 ± 0.85 g kg^{-1}, respectively, for KBG. Positive

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artifacts associated with OC sampling were evaluated and remedied with a two-filter system.

EC and OC accounted for almost two-thirds of $PM_{2.5}$ mass, while LG accounted for just

under 3% of the $PM_{2.5}$ mass. Since EFs of these pollutants generally decreased with

increasing combustion efficiency (CE), identifying methods of increasing the CEs of burns

would help reduce their emissions from agricultural field burning. PAH, OC and EC EFs are

comparable to other similar studies reported in literature. MP EFs appear dependent on the

stubble type and are lower than the EFs for hard and softwoods reported in literature,

possibly due to the lower lignin content in wheat and KBG.

Keywords: PAH; methoxyphenol; levoglucosan; elemental carbon; organic carbon;

emission factor; combustion efficiency.

3.2. INTRODUCTION

Combustion is one of the methods used to reduce post-harvest residues from wheat and

Kentucky bluegrass (KBG) fields in eastern Washington (WA) and northern Idaho (ID).

Over 45,000 ha of wheat and 20,000 ha of KBG were burned in these areas in 2002 (WA

DOE, 2004; ISDA, 2003). Emission factors (EFs: the pollutant mass emitted per unit mass

of dry stubble consumed by fire) are required for modeling the dispersion of smoke from

these fires and for inventorying pollutant emissions.

Pollutants in smoke from agricultural burning include, among others, fine particulate

matter ($PM_{2.5}$) and semi volatile organic compounds (SVOCs, present in solid and gas

phases). $PM_{2.5}$ is known to affect respiratory health (Roberts and Corkill, 1998; Mar et al.,

2004). Several polycyclic aromatic hydrocarbons (PAHs; classified as SVOCs) emitted

during combustion are carcinogenic and are associated with mutagenicity (Seinfeld and

Pandis, 1997; Roberts and Corkill, 1998; Ramdahl and Becher, 1982). EFs of these

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pollutants are required for modeling human exposure to them, with the intention of safeguarding public health.

Several methoxylated phenols (MPs; also classified as SVOCs), particularly syringyl and guaiacyl species, are used as markers of lignin combustion (Simpson et al., 2005; Simoneit, 2002). 1,6-anhydro-β-D-glucopyranose, commonly known as levoglucosan (LG), is often reported along with MP measurements, as it is considered a marker of cellulose pyrolysis, and predominates in the solid phase (Hays et al., 2002 and 2005; Schauer et al., 2001). MP and LG EFs are needed for developing source profiles for receptor models, which are tools for assessing the contribution of biomass burning to pollution episodes (Simoneit, 2002).

Elemental carbon (EC) and organic carbon (OC) can account for over 50% of the $PM_{2.5}$ mass in areas impacted by smoke from biomass burning (Reid et al., 2005; Seinfeld and Pandis, 1997). EC and OC emissions are inventoried since EC is an important species in radiative forcing, and OC includes species (such as PAHs) with toxicological properties. Knowledge of EC and OC EFs is required for compiling these inventories.

Recently we reported $PM_{2.5}$ EFs from wheat and KBG burning (Dhammapala et al., 2006). While PAH, MP and LG emissions from burning wood and forest debris are documented, a recent review paper (Lemieux et al., 2004) shows few studies reporting emissions of PAHs from agricultural burning. Additionally, two studies involving wheat and KBG burns [Air Sciences Inc. (A.S.I.), 2003 and 2004, respectively] in eastern WA and northern ID provide limited PAH data. We are only aware of one study (Hays et al., 2005) detailing the MP and LG emissions from agricultural burning, and part of the data in that study was collected during the experiments described in this paper.

Data on EC and OC emissions from agricultural burning are also scarce (Turn et al.,

1997; Hays et al., 2005). It is known that a positive sampling artifact may substantially bias OC measurements (Kirchstetter et al., 2001; Subramanian et al., 2004; Turpin et al., 1991). However literature reporting OC EFs from biomass burns (e.g. Turn et al., 1997; Christian et al., 2003) does not mention an artifact correction, and as a result, the accuracy of OC EFs is unknown.

The purpose of this work is to address these data needs by determining EFs of 19 PAHs (including all species on the former "priority PAH" list), 19 MPs (9 guaiacyl and 10 syringyl species, often reported in recent literature), LG, EC and OC from wheat and KBG stubble burning.

3.3.   METHODOLOGY

Irrigated winter wheat (*Triticum aestivum* L., variety Madsen) and non- irrigated KBG (*Poa pratensis* L.) stubble was collected from fields in eastern WA and northern ID, respectively, just prior to burn experiments. The moisture content in all stubble was approximately 9%. Burn experiments were conducted during May and August 2001 (Campaigns 1 and 2 respectively), August 2003 (Campaign 3) and July 2004 (Campaign 4), in an enclosed, well-mixed, flow-through test burn chamber located at the US EPA in Research Triangle Park, NC. During each burn, approximately 750g of stubble, arranged to mimic post- harvest field orientation, was ignited manually with a propane torch and the chamber door closed immediately. Pollutant concentrations, chamber air flow rates, chamber temperatures and stubble mass loss rates were measured for calculation of EFs.

3.3.1. Sampling

For each burn experiment, emissions were sampled for approximately 20 minutes, until stubble mass loss and smoldering combustion ceased. $PM_{2.5}$, CO_2, CO and hydrocarbon

sampling is described in detail Dhammapala et al. (2006). Particle phase SVOCs and LG

were sampled with a low volume (LV: 5 L min^{-1}; Airmetrics Inc., Eugene, OR) PM$_{2.5}$

sampler with 47 mm diameter Teflon filters (Whatman Inc., 40 μm thick, 2 μm pores).

Polyurethane foam (PUF) plugs (URG Corp., Chapel Hill, NC), with a diameter of 1.5 cm

and thickness of 3-4 cm, were placed in a silanized glass tube (Simpson et al., 2005)

downstream of the Teflon filters to trap gas phase SVOCs. Prior to use, PUFs were cleaned

twice in a Soxhlet extractor for 24 hours in a 1:1 mixture of acetonitrile and ethyl acetate.

Additional LV samplers with pre-heated (800 ºC for 12 hours) 47 mm diameter quartz filters

(Whatman Inc., thickness 0.45 mm) were used for sampling EC and OC.

The configurations of filters and PUFs in the LV samplers are shown in Figure 3.1. An

inventory of samples collected is provided in Table 3.1. During the Campaign 1 burns, a

dilution sampler was also operated to assess the chemical composition of PM$_{2.5}$ (see Hays et

al., 2005).

3.3.1.1   OC adsorption artifact

The adsorption of SVOCs on quartz filters gives rise to a positive OC sampling artifact,

and this is corrected by subtracting the SVOC collected on the QbT filter, from the OC on

the Q filter (Mader et al., 2003; Pang et al., 2002; Turpin et al., 1994; Eatough et al., 1993).

For the purpose of this document, we assume that there is no significant negative artifact

caused by SVOC volatilization off filters during sampling (Pang et al., 2002; Mader et al.,

2003). Since PAHs and MPs could be contained in the artifactual OC (Hays et al., 2005),

quartz filters were not analyzed for solid phase SVOCs.

3.3.2. Analytical methods

The samples from Campaigns 1, 2 and 3 were analyzed for 16 PAHs at Eastern

Washington University (EWU) in Cheney, WA, by gas chromatography and mass spectrometry (GC-MS). Samples from Campaign 4 were analyzed for 20 PAHs, 19 MPs and LG at the University of Washington (UW) in Seattle, WA, also by GC-MS. The GC-MS at UW was operated in selective ion mode and had a lower detection limit than the instrument at EWU, which was run in full scan mode.

All glassware was silanized prior to use during SVOC analysis. The procedures for extraction, sample preparation and analysis of PAHs, LG and MPs have been described previously (Simpson et al., 2004 and 2005; Dills et al., 2006). Briefly, samples were spiked with a known mass of deuterated standards and extracted by sonicating in 30 mL ethyl acetate containing 0.5 % (v/v) triethylamine (TEA). Extracts were turbo- evaporated down to 0.5 mL and the relevant internal standards added. For LG and MP analyses, a portion of the extract was then derivatized with 10% (v/v) N-trimethylsilylimidazole, and a 4:3 solution of acetic anhydride and TEA, respectively. Samples were then injected into the GC-MS.

For EC and OC quantification, rectangular 1.5 cm^2 punches of the quartz filters were analyzed with a Thermal Optical Transmittance (TOT) carbon analyzer (Sunset Labs Inc., Tigard, OR). The temperature program used was the NIOSH reference method 5040 (NIOSH, 1999), with some modifications (Pang et al., 2002).

3.4.   DATA VALIDITY AND QA/ QC MEASURES

Secondary OC can be formed during downwind transport (Turpin et al., 1991). Reactions between solid phase PAH and O_3, and gas phase PAH and OH radicals can both result in PAH lifetimes of less than an hour (rate constants from Pöschl et al., 2001; Alebić-Juretić et al., 1990; Calvert et al., 2002). MPs have been reported to react with PAHs

(Kjällstrand and Petersson, 2001; McDow et al., 1994). Therefore EFs of organic species presented here are valid at the point of emission only.

Laboratory blanks were analyzed with every batch of field samples. Analyte concentrations in these blanks were either below detection limits, or were lower than the corresponding analyte concentrations in background samples from the chamber experiments. Based on the average of all individual species, the precision of field duplicates was 22% for both PAHs (8 sample pairs) and MPs (4 sample pairs). For LG, the precision was 11%, based on 1 sample pair. The relative standard deviation (RSD) of triplicate laboratory analyses was 14% (n=12), 12% (n=6) and 6% (n=1) for PAHs, MPs and LG, respectively.

The TOT method for EC and OC analysis assumes that the sample is evenly distributed across the quartz filter. TOT analyses on duplicate punches obtained from the same filter showed a high degree of precision (average 3.0%, based on 26 filter pairs), confirming the applicability of the assumption.

3.4.1. Extraction and retention efficiency tests

The extraction efficiency is the ratio of deuterated SVOC or LG mass measured by the GC-MS, to the mass of deuterated compound amended onto the sample prior to extraction. Average extraction efficiencies were 74±32% (PAH- Teflon), 74±39% (PAH- PUF), 66±27% (MP- Teflon), 104±69% (MP- PUF) and 79±3% (LG- Teflon). PAH and MP extraction efficiencies are based on the average of all individual species, and the uncertainties are the RSDs. Data reported henceforth are corrected for sample-specific and compound-specific extraction efficiencies, thus accounting for analytical losses.

Retention efficiencies (i.e. a measure of sampling and storage losses) were evaluated by spiking Teflon filters and PUFs, with deuterated PAH and MP mixtures prior to sampling.

They were then analyzed as regular samples. Average PAH retention efficiencies were 87±28% [Teflon filters, molecular weight (MW) $\geq$202 g mol^{-1} only] and 117±41% (PUFs, excluding d8-naphthalene, for which the retention efficiency was <20%). PAH and MP retention efficiencies are based on the average of all individual species, and the uncertainties are the RSDs All further references to "solid phase PAHs" imply those with MW $\geq$202 g mol^{-1}. References to "solid + gas phase PAHs" imply the sum of all measured PAHs, except naphthalene, collected on Teflon filters and PUFs. The average MP retention on PUFs was 81±39%. MP retention efficiencies on Teflon filters were not evaluated since MPs are expected to predominate in the gas phase (Schauer et al., 2001). Also LG retention efficiencies were not evaluated as LG is mainly present in the solid phase (Simoneit, 2002).

3.4.2. Degradation of PAHs by O_3 during sampling

When sampling PAHs, O_3 at ambient concentrations have been found to degrade PAHs deposited on the filters (Pöschl et al., 2001; Alebić-Juretić et al., 1990), causing PAH EFs to be underestimated. However O_3 levels [measured with a TECO O_3 analyzer, model 49 (Thermo Electron Corp., MA)] in the US EPA chamber during burns were below the detection limit of 1 ppb. Nitric oxide produced by the fires (Hurst et al., 1994) is expected to titrate out the ~40 ppb ambient O_3 entering the chamber, and the pollutant residence time in the chamber is insufficient for fresh O_3 formation.

3.5. CALCULATIONS

Calculation of combustion efficiency (CE: the fraction of carbon released as CO_2) and EFs including assumptions therein are described in Dhammapala et al. (2006). Background corrected pollutant concentrations are used for this purpose. The systematic errors of the SVOC and LG EFs were estimated (based on propagation of errors) to be ±30%, while EC

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and OC EFs are within ±25%. All uncertainties of results are reported henceforth as 95% confidence intervals.

3.6. RESULTS AND DISCUSSION

3.6.1. Polycyclic Aromatic Hydrocarbons

The sums of EFs of 19 PAHs in both gas and particle phases were 17 ± 8.2 mg kg^{-1} and 21 ± 15 mg kg^{-1} for wheat and KBG, respectively. EFs for individual PAHs are included in Table 3.A1 of the electronic supplementary material. The negative correlations between PAH EFs and CE are expected since PAHs are products of incomplete combustion (Figure 3.2). Although gas phase PAH EFs from KBG (Figure 3.2b) are not well correlated with CE, the wheat data have a R^2 of 0.65.

Some heavier species that are expected to predominate in the solid phase are in fact present in the gas phase (see data in Table 3.A1). This may be due to the effect of chamber temperature (which changes throughout the burn cycle) on phase partitioning (Jenkins et al., 1996a and 1996b). The solid and gas phase PAHs may not always equilibrate in the short time between their formation and sampling in the chamber.

Tables 3.2 and 3.3 summarize and compare the EFs found in this study, against those appearing in literature. Comparison of SVOC EFs against literature is not straightforward since different studies report EFs of different SVOCs. Listed in Table 3.3 is the sum of individual species reported, compared against the same species measured in this work. Little or no PAH EFs have been reported for wheat or KBG stubble burning. Wheat and KBG PAH data are in reasonable agreement with other data for wheat (Jenkins et al., 1996a; Hays et al., 2005) when CE differences are taken into account. But wheat and KBG EFs are not always similar to those from burning other types of biomass. Though PAH EFs from rice

straw (Korenaga et al., 2001) are comparable, higher PAH EFs have been reported for barley, foliar fuels and fireplace woods.

Higher PAH EFs from barley might be due, in part, to the fact that the barley stubble used by Ramdahl and Møller (1983) had a moisture content of 15%, whereas the wheat and KBG used in this study had a moisture content of 9%. Hays et al. (2002- foliar fuels) and Schauer et al. (2001- fireplace woods) both used dilution samplers and quartz filters upstream of PUFs when sampling. We removed the effect of dilution on phase equilibrium and eliminated the quartz filter (adsorption) artifact by summing the EFs of both phases. It is likely that woody fireplace fuels (Schauer et al., 2001)) burn at lower CEs. Foliar fuels burned by Hays et al. (2002) had more moisture (8- 44%) than wheat and KBG stubble. These factors could partly explain the higher PAH EFs in both foliar fuels and fireplace woods.

3.6.2. Methoxyphenols

The sums of EFs of 19 MPs in both phases were 35 ± 24 mg kg^{-1} and 79 ± 36 mg kg^{-1} for KBG and wheat, respectively. EFs for individual MPs (see Table 3.A2 of the electronic supplementary material) show that most of the lighter MPs are in the gas phase.

Although combined solid + gas phase MP EFs appear to show negative correlations with CE (Figure 3.3), these relationships are not very strong. Figure 3.3 also shows that lower CE KBG burns emit less MPs than the higher CE wheat fires. Because MPs are derived from lignin pyrolysis, the lower lignin content in KBG (1.8%- Sartain, 2004) compared to wheat (11%- Ibrahim, 1998) would partly explain the lower MP EFs from KBG, in spite of lower CEs in the latter.

Tables 3.2 and 3.3 summarize and compare the MP EFs. Little or no MP EFs have been

reported for wheat or KBG stubble burning. MP EFs from foliar fuels (Hays et al., 2002) and fireplace woods (Schauer et al., 2001) are higher than wheat and KBG EFs measured in this work. In addition to potential CE differences (described in Section 3.6.1), the high MP EFs from the hard and softwoods used in fireplaces (Schauer et al., 2001) could also be caused by the higher lignin content [20±4% and 28±3% lignin in hard and softwoods, respectively (Ibrahim, 1998)].

3.6.3. Levoglucosan

LG EFs are 150±130 mg kg^{-1} for wheat and 350±510 mg kg^{-1} for KBG. As expected the LG EFs show a strong negative correlation with CE (Figure 3.4). LG in wheat and KBG accounts for 2.3±1.5% and 2.7±2.0% of the PM$_{2.5}$, respectively. Though it is difficult to compare KBG EFs due to the wide uncertainties (partly a consequence of having only 3 samples), the summary of EFs and comparison in Table 3.2 shows that the LG EFs for wheat are similar to wheat data of Hays et al (2005). CE differences may partly explain the lower wheat EFs compared to other types of biomass.

3.6.4. EC and OC

3.6.4.1 KBG

The EC EF was 0.63±0.056 g kg^{-1} and the artifact-corrected OC EF was 6.9±0.85 g kg^{-1}. Both EC and OC show a negative trend with CE (Figure 3.5). EC + artifact-corrected OC accounted for 63±1.9% of the PM$_{2.5}$ mass. The OC EF vs. CE relationship is more scattered than the corresponding EC data, possibly caused by varying amounts of gas phase OC condensing onto solid phase OC (due to differences in chamber temperature). The positive OC artifact was 5.0±0.8% of the uncorrected OC.

3.6.4.2   Wheat

The EC EF was 0.35 ± 0.16 g kg^{-1} and the artifact-corrected OC EF was 1.9 ± 1.1 g kg^{-1}. As with KBG, EC and OC EFs decrease with increasing CE (Figure 3.5). These confidence intervals are wider than those reported for KBG, and are a consequence of having fewer samples (see Table 3.1). EC + artifact-corrected OC accounted for $63\pm5.3\%$ of the PM$_{2.5}$ [PM$_{2.5}$ EFs for wheat were nearly a factor of 4 lower than KBG (Dhammapala et al., 2006)]. The QbT artifact accounted for $20\pm5.5\%$ of uncorrected Q OC.

Table 3.2 summarizes EC and OC EFs, and compares them against those found in literature. EFs from biomass burned in woodstoves are at the lower limit of those found in this study, and this is expected since woodstoves are designed to produce low emissions. References cited in Table 3.2 do not state whether OC data therein have been corrected for adsorption artifacts. Nevertheless EC and OC EFs evaluated in this study appear reasonably consistent with data reported in literature.

3.7.   CONCLUSIONS

This work presents some of the first measurements of EFs of SVOCs from KBG stubble burning. On average, the PAH and MP EFs for combined solid + gas phases are 17 ± 8.2 mg kg^{-1} and 79 ± 36 mg kg^{-1} respectively for wheat, and 21 ± 15 mg kg^{-1} and 35 ± 24 mg kg^{-1} respectively for KBG. LG, particulate EC and artifact-corrected OC EFs are 150 ± 130 mg kg^{-1}, 0.35 ± 0.16 g kg^{-1} and 1.9 ± 1.1 g kg^{-1} respectively for wheat, and 350 ± 510 mg kg^{-1}, 0.63 ± 0.056 g kg^{-1} and 6.9 ± 0.85 g kg^{-1} respectively for KBG. Since EFs of many of these pollutants are inversely correlated with CE, identifying methods of increasing the CEs of burns would help reduce the SVOC emissions from agricultural field burning.

Naphthalene (MW 128) cannot be sampled effectively with Teflon filters or PUFs under

these conditions, and alternative sampling methods need to be used. The importance of correcting for the adsorption of OC on quartz filters is underscored by the fact that this artifact could positively bias the OC EFs by between 2- 26%.

3.8.   ACKNOWLEDGEMENTS

3.9.   REFERENCES

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3.10. LIST OF FIGURES

| PM₂.₅ | PM₂.₅ | PM₂.₅ |

$PM_{2.5}$

Teflon filter (PM$_{2.5}$, solid phase SVOC, LG)

PUF (gas phase SVOC)

Config. 1

$PM_{2.5}$

Teflon filter (duplicate PM$_{2.5}$)

Quartz filter behind Teflon (QbT) (OC artifact)

Config. 2

$PM_{2.5}$

Quartz filter (Q) (EC and OC)

Config. 3
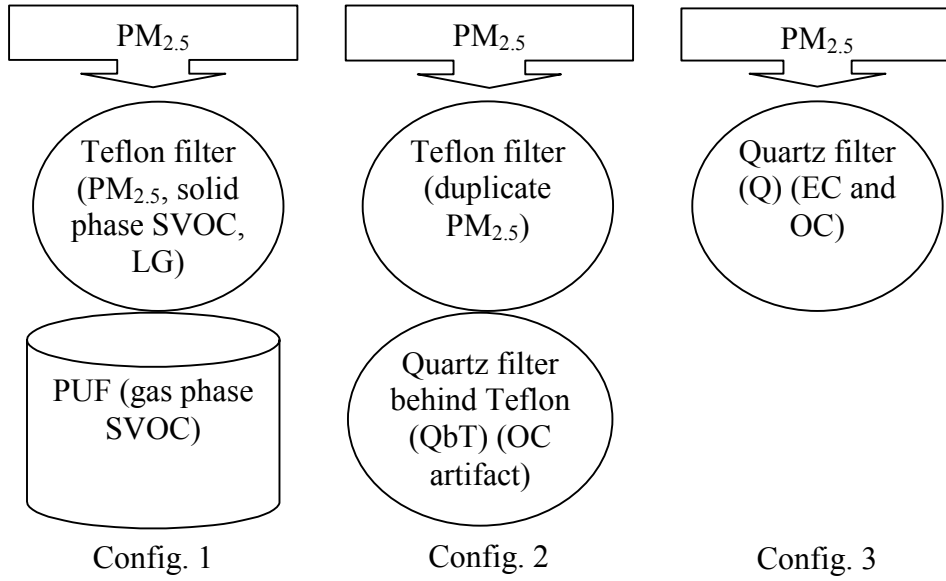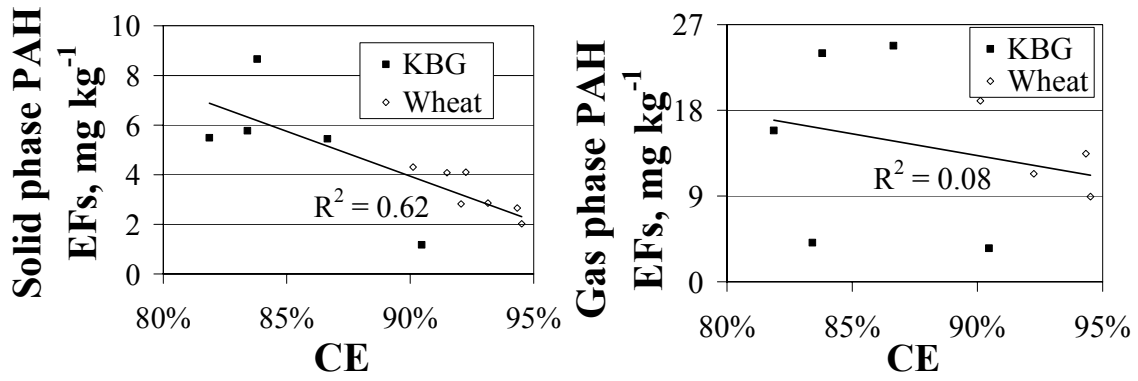
Figure 3.1.

Figure 3.2.

Figure 3.3.

57
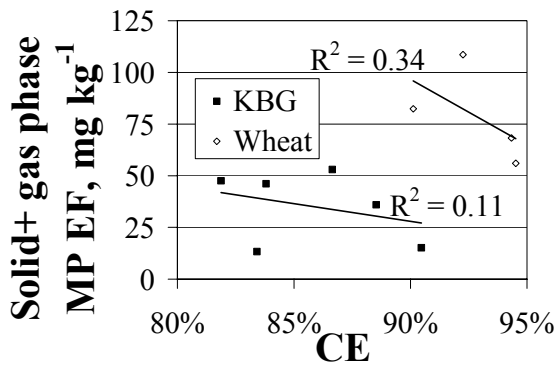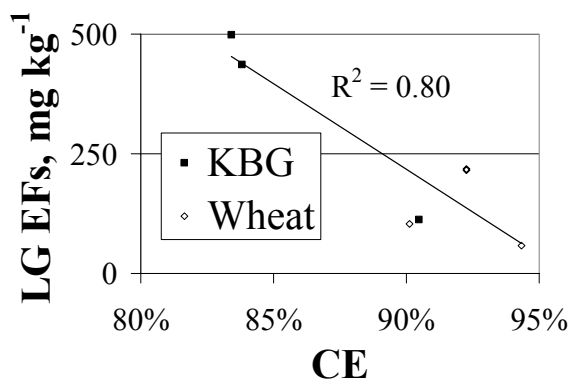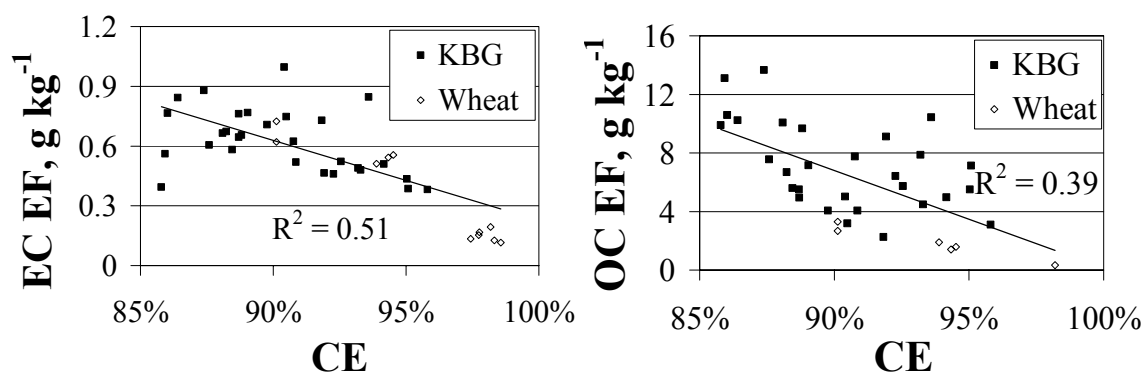
Figure 3.4.

Figure 3.5.

Table 3.1:   Number of samples collected using LV samplers. The numbers in square

brackets are the # burn experiments conducted. Numbers in parentheses are the # of

Teflon filters combined prior to analysis at EWU, to obtain a detectable PAH mass.

	Wheat stubble			KBG stubble	
	Campaign 1 [30]	Campaign 2 [31]	Campaign 4 [6]	Campaign 3 [30]	Campaign 4 [6]
Teflon |Config. 1	30 (5)	31 (6)[a]	6	85[b]	6
PUF |Config. 1	-	-	4	8[b]	6
Teflon| Config.2	1[c]	[c]	6	33	6
QbT| Config.2	1[c]	[c]	5	29	5
Q| Config.3	6[c]	[c]	5	33	5

[a] Teflon filters from the last 7 burns were combined.

[b] All SVOC data from the KBG burns of Campaign 3 were lost.

[c] Some samplers malfunctioned and therefore limited the number of samples collected.

Table 3.2:   Summary of PAH, MP, LG, OC and EC EFs for wheat and KBG

	Wheat	KBG	Literature[a]
$\Sigma 19$ PAHs, mg kg^{-1}	17±8.2[b] (CE 93±3.3%)	(CE 21±15[b] 85±4.2%)	(CE See Table 3.3
$\Sigma 19$ MPs, mg kg^{-1}	79±36[b] (CE 93±3.3%)	(CE 35±24[b] 85±4.2%)	(CE
LG, mg kg^{-1}	150±130 92±2.7%)	(CE 350±510 86±9.8%)	(CE 123[c], 65- 356[d], 303- 1,188[e], 706- 1,940[f]
OC, g kg^{-1}	1.9±1.1 94±3.2%)	(CE 6.9±0.85 90±1.0%)	(CE 1.23[c], 0.5-1.9[d], 8.0-27.8[e], 3.0-5.3[f], 2.1[g], 1.0-15.7[h]
EC, g kg^{-1}	0.35±0.16 96±2.1%)	(CE 0.63±0.056 90±1.0%)	(CE 0.52[c], 0.08-0.3[d], 0.2-1.3[e], 0.8-1.9[f], 0.79[g], 0.04-1.5[h], 0.5-1.2[i]

[a.] When several fuels are reported, the EF range is presented for comparison.

[b.] SVOC data from Campaign 4, reported as the sum of solid and gas phases.

[c.] Hays et al. (2005), wheat, (Campaign 1)   [d.] Fine et al. (2004), woodstoves

[e.] Hays et al. (2002), foliar fuels   [f.] Schauer et al. (2001), fireplace woods

[g.] Turn et al (1997), wheat   [h.] Christian et al. (2003), Several woods-

[i.] Ward and Hardy (1991), logging slash   -often burned in Zambia and Indonesia

Table 3.3:   Comparison with literature: The sum of SVOC EFs in the solid + gas phases, unless otherwise stated. Numbers in parentheses are the # of SVOCs summed.

Reference	ΣSVOC EFs[a], mg kg^{-1}	This work[b], mg kg^{-1}	
		Wheat	KBG
PAHs			
Jenkins et al. (1996a), wheat, CE ~ 85%	20 (17)	16	20
Hays et al. (2005), wheat, dilution sampling during Campaign 1, PM$_{2.5}$ on quartz filter	2 (14)	3.3	5.3
Korenaga et al. (2001), PAH on total PM, rice straw, 10% stubble moisture.	2 (7)	1.9	3.9
Ramdahl and Møller (1983), barley	36 (17)	16	20
Hays et al. (2002), foliar fuels	8- 26 (5)	8.4	7.6
Schauer et al. (2001), fireplace woods	34- 74 (17)	16	21
MPs			
Hays et al. (2005), as above	5 (13)	6.8	5.4
Hays et al. (2002), as above	372- 1,167 (10)	48	26
Schauer et al. (2001), as above	1,338- 1,682 (17)	78	35

[a.] When several fuels are reported, the EF range is presented for comparison.

[b.] Sum of the same SVOCs in the appropriate phase(s). When solid phase PAHs are compared, only those with MW $\geq$202 g mol^{-1} are considered.

3.11. ELECTRONIC SUPPLEMENTARY MATERIAL

Table 3.A1: Average PAH EFs broken down by species. Only PAHs with MW $\geq$202 g mol^{-1} are reported in the solid phase.

PAH (molecular weight, g mol^{-1})	Wheat EFs, mg kg^{-1}			KBG EFs, mg kg^{-1}		
	Solid	Gas	Total	Solid	Gas	Total
Acenaphthylene (152)		3.4	3.5		6.6	6.9
Acenaphthene (154)		0.15	0.22		0.56	0.60
Fluorene (166)		0.77	0.83		1.5	1.6
Phenanthrene (178)		4.0	4.1		3.5	4.0
Anthracene (178)		1.4	1.4		0.95	1.2
Fluoranthene (202)	0.14	1.3	1.4	0.81	0.38	1.2
Pyrene (202)	0.18	1.1	1.3	0.76	0.30	1.1
Benz[a]anthracene (228)	0.61	0.26	0.87	1.1	0.054	1.1
Chrysene+ triphenylene (228)	0.25	0.049	0.30	0.52	0.024	0.55
Retene (234)	0.11	0.082	0.19	0.11	0.038	0.15
Benzo[b]fluoranthene (252)	0.47	ND	0.47	0.31	ND	0.31
Benzo[k]fluoranthene (252)	0.51	ND	0.51	0.44	ND	0.44
Benzo[e]pyrene (252)	0.15	0.14	0.29	0.22	0.12	0.35
Benzo[a]pyrene (252)	0.28	0.10	0.39	0.42	0.050	0.47
Perylene (252)	0.29	0.15	0.45	0.18	0.17	0.35
Indeno[1,2,3-cd]pyrene (276)	0.032	ND	0.032	0.054	ND	0.054
Benzo[g,h,i]perylene (276)	0.083	ND	0.083	0.19	ND	0.19
Dibenzo[a,h]anthracene (278)	0.12	ND	0.12	0.14	ND	0.14
Coronene (300)	0.044	ND	0.044	0.056	ND	0.056
Σ19 PAHs	3.3	13	16	5.3	14	20

- ND = Not detected in any samples.
- Except for NDs, individual non-detects are treated as half the minimum detection limit in calculations.

- The Σ19 PAHs (last row) is the sum of the averages of all species. This differs slightly from data in Table 3.3; the latter is the average of the sum of all species and includes NDs.

Table 3.A2:   Average MP EFs broken down by species.

MP (molecular weight, g mol^{-1})	Wheat EFs, mg kg^{-1}			KBG EFs, mg kg^{-1}		
	Solid	Gas	Total	Solid	Gas	Total
Guaiacol (124)	0.034	0.73	0.76	0.04	1.1	1.1
Methyl Guaiacol (138)	0.050	0.52	0.57	0.03	3.8	3.8
Ethyl Guaiacol (152)	0.0073	1.9	2.0	0.08	2.3	2.4
Vanillin (152)	0.91	4.9	5.8	1.06	2.5	3.6
Syringol (154)	0.030	6.9	7.0	1.46	ND	1.5
Eugenol (164)	0.013	2.5	2.5	0.03	2.5	2.5
Propyl guaiacol (166)	0.010	1.0	1.0	0.10	1.1	1.2
Acetovanillone (166)	0.083	5.6	5.7	0.44	0.80	1.2
Methyl syringol (168)	0.046	9.0	9.0	0.41	3.0	3.4
Coniferyl aldehyde (178)	4.0	0.11	4.2	0.78	0.019	0.79
Guaiacyl acetone (180)	0.18	11	11	0.83	1.8	2.6
Ethyl syringol (182)	0.033	12	12	0.23	4.1	4.3
Syringaldehyde (182)	1.7	1.9	3.6	0.76	2.6	3.4
Allyl syringol (194)	0.046	3.6	3.7	0.39	1.3	1.7
Propyl syringol (196)	0.019	0.84	0.86	0.19	0.33	0.52
Acetosyringone (196)	2.3	3.9	6.2	0.10	0.51	0.61
Sinapyl aldehyde (208)	1.4	ND	1.4	0.03	0.078	0.11
Propyl syringone (210)	0.65	0.29	0.94	0.10	0.033	0.14
Butyl syringone (224)	0.11	ND	0.11	0.025	ND	0.025
Σ19 MPs	12	67	79	7.1	28	35

- ND = Not detected in any samples.
- Except for NDs, individual non-detects are treated as half the minimum detection limit in calculations.

4   EMISSION FACTORS FROM WHEAT AND KENTUCKY BLUEGRASS STUBBLE BURNING: COMPARISON OF FIELD AND SIMULATED BURN EXPERIMENTS

Emission factors from wheat and Kentucky bluegrass stubble burning: comparison of field and simulated burn experiments

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4.1.   ABSTRACT

Emission factors (EFs) of $PM_{2.5}$, CO, elemental carbon (EC), particulate organic carbon (OC), polycyclic aromatic hydrocarbons (PAHs) and methoxyphenols (MPs) from post-harvest burning of wheat and Kentucky bluegrass (KBG) stubble were evaluated in a series of field burns. Integrated smoke samples were collected at ground level, upwind and downwind of the fires, and EFs were determined with the carbon balance method (validated during previous chamber experiments). These EFs were compared against EFs evaluated from previously conducted chamber burns, to determine how well the latter represent field scenarios. In general, when combustion efficiency (CE) differences were taken into account, a reasonable degree of agreement was observed between emission factors measured in the field and in the chamber, except for EC and solid+ vapor phase PAHs, both from wheat burns. EC and PAHs from wheat burns were seen in higher amounts in the chamber, although the PAH data are in agreement at CEs> 90%. Poor EC and OC EF- CE correlations in chamber data make the comparison with KBG field data difficult. The particulate organic matter/ OC ratios were 2.1±1.3 (wheat) and 1.9 (KBG), and were close to those observed

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during chamber experiments. Though CO and CH$_4$ EFs evaluated from ground-based samples differed from those collected on board a light aircraft, EF- CE relationships were similar. This underscores the importance of determining both the CEs and EFs simultaneously.

Keywords: wheat, Kentucky bluegrass, field burn, combustion efficiency, emission factor

4.2. INTRODUCTION

The post harvest burning of agricultural residue produces several atmospheric pollutants. Recently we reported emission factors (EFs) of PM$_{2.5}$, CO, hydrocarbons (Dhammapala et al., 2006a), elemental and particulate organic carbon (EC and OC), selected polycyclic aromatic hydrocarbons (PAHs) and methoxyphenols (MPs) (Dhammapala et al., 2006b), emitted from wheat (*Triticum aestivum* L.) and Kentucky bluegrass (KBG, *Poa pratensis* L.) stubble burning. Those experiments were conducted in a test burn chamber.

In contrast with combustion in burn chambers, combustion in the field is affected by several additional variables including local meteorology, terrain, cropping and burning practices, stubble moisture content and fire characteristics such as temperature, intensity, spread and burn rate. Since several of these factors could affect the combustion efficiency (CE) of the fire and therefore EFs (A.S.I., 2003; Jenkins et al., 1996; Carroll et al., 1977), it is necessary to understand how well chamber burns represent field scenarios.

Data from our above-mentioned chamber experiments cannot be readily compared against field data in literature, since few field studies have been conducted to determine EFs from wheat and KBG burning (Darley et al., 1974; Boubel et al., 1969; A.S.I. 2003 and 2004). These few studies focus mostly on particulate matter, CO and hydrocarbon

emissions, and the A.S.I studies provide very limited data on solid phase PAH emissions. We are unaware of field studies reporting EFs of EC, OC, MPs (solid or vapor phase) or vapor phase PAHs, from wheat and KBG burns.

The purpose of this work is to compare the EF- CE relationships for $PM_{2.5}$, CO, EC, OC, MPs and PAHs from wheat field burns (conducted in eastern WA) and KBG field burns (conducted in northern ID), with corresponding measurements previously reported from the burn chamber. Ground- based smoke samples collected during field studies may be biased toward smoldering emissions on account of lower plume buoyancy (Hurst et al., 1994; Ward et al., 1992). Ideally smoke samples need to be representative of the entire plume. Therefore, a secondary objective of this work is to compare EFs calculated from ground-based field samples, against EFs evaluated by collecting samples on board a light aircraft.

4.3.   EXPERIMENTAL

Six wheat and two KBG field burns were conducted between August 2004 and August 2005. Field sizes ranged from 13- 80 ha. Samples of pre burn stubble and post burn ash were collected from at least 10 randomly chosen locations in the field, finely ground, composited and analyzed for carbon content using a CNS2000 total carbon analyzer (LECO Corporation, St. Joseph, MI). Ambient temperature and pressure during field burns were recorded.

Integrated smoke samples were collected at ground level, upwind and downwind of the fires. Downwind sampling commenced at the time of ignition and continued until smoldering had almost ended. Sampling times ranged from 40 minutes to 2 hours. Downwind sites were typically a few meters away from the field edge of the burn area. Upwind samplers, located at least 200m away from the burn, started before and ended after

the fire. The concentration of pollutants generated by the fire is the difference in concentrations between upwind (background) and downwind samples.

Integrated gaseous samples (for CO_2, CO and CH_4 analysis) were collected in 30 mL plastic syringes, mounted on ground-based syringe samplers and filled at a constant rate over 20 minutes. $PM_{2.5}$, PAH, MP, EC and OC sampling methods are described in detail in Dhammapala et al. (2006a and 2006b). Briefly, integrated $PM_{2.5}$ and solid phase semivolatile organic compounds (SVOCs; includes PAHs and MPs) were sampled on Teflon filters, while vapor phase SVOCs were trapped on Polyurethane foam (PUF) plugs placed downstream of Teflon filters. $PM_{2.5}$ samples were also collected onto Quartz filters (abbreviated QF), to determine the EC and OC fractions therein. All OC data reported here have been corrected for the adsorption artifact on QF (Turpin et al., 1994), using a separate quartz filter placed behind a Teflon filter (abbreviated TQ).

A single engine Cessna C-172 aircraft was used to obtain smoke samples for calculation of EFs from airborne measurements. Grab samples were manually drawn into syringes while flying through the plume, between 100 and 2100m (median 1100m) above ground level. $PM_{2.5}$ measurements from the aircraft were not possible since an isokinetic sampling inlet was unavailable. To minimize secondary atmospheric processes and stay well above background concentrations, aircraft based sampling was conducted relatively close to the fire. Table 4.1 lists pertinent experimental details.

All syringe samples were analyzed for CO_2, CO and CH_4 using a Carle SX 270 Gas Chromatograph (1m Molecular Sieve 5A 45/ 60 mesh column at 90ºC, N_2 carrier gas flowing at 35 mL min^{-1}) equipped with a methanizer (400ºC) and a flame ionization detector (FID). Analytical methods for $PM_{2.5}$, PAH, MP, EC and OC are described in detail in

Dhammapala et al. (2006a and 2006b). Briefly, $PM_{2.5}$ mass was determined gravimetrically. Teflon filter and PUF extracts were analyzed by gas chromatography- mass spectrometry (GC-MS) for PAHs and MPs. Teflon filter extracts were also analyzed for levoglucosan, and the results are reported in Jimenez et al., (2006). Quartz filters were analyzed for EC and OC on a thermal optical transmittance (TOT) analyzer.

As reported in Dhammapala et al., (2006a and 2006b), the chamber burns were conducted using 750g wheat or KBG stubble, arranged to mimic field orientations in eastern Washington (WA) and northern Idaho (ID), respectively.

4.3.1. Calculation of EFs

The method used for calculating EFs in the field (A.S.I., 2003; Hurst et al., 1994; Andreae and Merlet, 2001; Radke et al., 1988; Nelson, 1982) is presented in equation 1. The method is based on the conservation of C in the biomass, and does not require pre-and post-burn weighing of biomass.

$$EF_x \ (g \ kg^{-1}) = \frac{\Delta C_x \times \left(1,000 \ g \ kg^{-1}\right) \times C_{fraction}}{\left(\Delta CO_{2}{-}_C + \Delta CO{-}_C + \Delta CH_{4}{-}_C + \Delta PM_{2.5}{-}_C\right)} \qquad (1)$$

Where EF_x = Emission factor in g of pollutant X per kg dry stubble burned.

ΔC_x = Concentration of pollutant X in excess of the background, $mg \ m^{-3}$.

$\Delta CO_{2}{-}_C$ $(mg \ m^{-3})$ = [mass fraction of C (w/w) in CO_2 (i.e. 12/44)] × [average background-corrected CO_2 concentration $(mg \ m^{-3})$], etc for all species.

$C_{fraction}$ = mass fraction of C in dry stubble

This method assumes the following:

1. Physico-chemical processes between emission and sampling are considered to have negligible effect on the pollutant concentrations. All pollutants are present in a unit

volume of air sampled, in the same proportion in which they were produced by the fire (Nelson, 1982; Radke et al., 1988). Since the time between pollutant generation and field sampling ranges from seconds to minutes, it is unlikely that secondary processes cause a significant impact.

2. Pre and post burn biomass have similar $C_{fractions}$ (Nelson, 1982; A.S.I., 2003). Though the $C_{fraction}$ in ash was found to be 5.8±4.3% less than that of stubble, data in A.S.I., 2003 and 2004, and Dhammapala et al., 2006a show that unburned stubble accounts for 95% (wheat) and 94% (KBG) of the post burn biomass. Hence the $C_{fraction}$ in post burn biomass is approximately equal to that of pre burn stubble.

3. All carbon in the biomass consumed by fire is released into the atmosphere during combustion, and can be accounted for by measuring concentrations of CO_2, CO, total hydrocarbons and $PM_{2.5}$ in the plume (Radke et al., 1988; Andreae and Merlet, 2001). This assumption was validated by performing a carbon balance closure during the burn chamber experiments (Dhammapala et al., 2006a). For the field experiments, we were only able to measure CH_4 instead of total hydrocarbons, but determined that this substitution altered the carbon balance, CEs and EFs by <3%.

4. The background concentrations measured upwind are representative of ambient air impacting the field. During the wheat field burns in Connell, WA, the temporal and spatial variation of the background was assessed by placing 3 sets of samplers around the field at different upwind locations. The average relative standard deviation (RSD) of background CO_2, CO, CH_4 and $PM_{2.5}$, measured over 2 hours was 2.8%. Further, the average RSD of CO_2, CO and CH_4 in all airborne and ground-based background samples was 2.7%. Therefore this assumption was deemed valid.

4.3.2. QA/ QC measures

Ten syringes were pre-filled with CO_2, CO and CH_4 calibration standards, transported to and from the field, stored for 2 months and analyzed. The change in CO_2, CO and CH_4 concentrations averaged 1.9%. The precision of field duplicates for each parameter is shown in Table 4.2.

PAHs and MPs are subject to larger uncertainties than the other pollutants due to the increased complexity of analytical procedures for these analytes. PAH and MP samples were spiked with deuterated mixtures of PAHs and MPs prior to analysis. All PAH and MP results reported here have been corrected for losses during analysis, using the fractional recoveries of the spiked deuterated compounds.

When comparing ground and aircraft based EFs, the combustion efficiencies (CE) and emission factors (EFs) were calculated with CO_2, CO and CH_4. Although $PM_{2.5}$ was monitored on the ground, it is omitted from the calculations to facilitate comparison with aircraft measurements. The omission of non- methane hydrocarbons and $PM_{2.5}$ results in the CEs and EFs being overestimated by no more than 5%.

Atmospheric O_3 has been observed to react with PAHs on samples collected on filter substrates (Pöschl et al., 2001; Peltonen and Kuljukka, 1995; Finlayson- Pitts and Pitts, 2000), resulting in underestimation of PAH EFs. However it is unlikely that sufficient O_3 would be formed in the plume, during the short time between emission and sampling. Since biomass fires release NO (Hurst et al., 1994), it is likely that ambient O_3 present would be removed by reacting with NO.

Because benzo[a]pyrene (b[a]p) is considered to be more photochemically reactive than benzo[e]pyrene (b[e]p), the b[a]p/ b[e]p ratio has been used to assess if smoke is

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subject to photochemical degradation during transport (Finlayson- Pitts and Pitts, 2000). We found that b[a]p/ b[e]p ratios in the chamber and field were 1.4±0.2 and 1.5±0.2 respectively. This suggests that PAHs were not degraded appreciably during the short time between emission and field sampling. MP degradation during transport was assumed to be negligible.

For field experiments, based on propagation of errors, $PM_{2.5}$, CO, CH_4, EC and OC EFs are estimated to be within ±20%, while SVOC EFs are within ±30%.

4.4. RESULTS AND DISCUSSION

The trendlines and R^2 values shown in the following figures pertain to the chamber experiments described in our previous manuscripts (Dhammapala et al., 2006a and 2006b), and cover the CE range seen therein. The CEs encountered in the field appear lower than those seen during chamber burns. Chamber EF- CE data were extrapolated by way of linear regression, to obtain EFs at the CE's encountered in the field. Extrapolated EFs expressed as a percentage of EFs measured in the field are presented in Table 4.3. Statistical significance testing was not conducted on account of the few data points. KBG data should be interpreted with caution since only two field burns could be conducted. The concentrations of each pollutant measured upwind and downwind of burns are presented in Table 4.A1 of the Electronic Supplementary Material.

4.4.1. CO and $PM_{2.5}$

The CO EF- CE relationships (Figure 4.1a) observed for both wheat and KBG in the field are similar to the CO EF- CE relationship observed for wheat in the chamber. On average, the extrapolated chamber EFs were 104% of field EFs for wheat, and 108% for KBG. The chamber experiments with KBG yielded lower CO EFs, for an unknown reason.

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The $PM_{2.5}$ EF- CE relationships are shown in Figure 4.1b. On average, the extrapolated chamber EFs were 78% of field EFs for wheat, and 83% for KBG.

4.4.2. EC and OC

EC EFs from wheat field burns are lower than the chamber (Figure 4.2a; extrapolated chamber EFs are 229% of field EFs). These differences may be partly caused by the TOT incorrectly assigning the EC- OC split (Reid et al., 2005). This could affect samples with high EC loadings to a greater extent, leading to the overestimation of EC EFs from chamber burns. Since OC EFs are larger than EC EFs, the former may not be significantly affected by the mis-assigned carbon.

The artifact corrected OC EF- CE relationships (Figure 4.2b) for wheat in the chamber and field are comparable except for two field measurements (circled in Figure 4.2b). These were traced to two background samples with high OC concentrations, possibly caused by contamination. When these two data points were omitted, extrapolated wheat chamber OC EFs were 91% of field EFs.

For KBG, when one data point (circled in Figure 4.2b) with a high OC background concentration was omitted, the extrapolated chamber EFs were 176% and 114% of the field EFs for OC and EC, respectively. However KBG OC and EC data should be interpreted with caution because of the few data points as well as the poor EF- CE correlations seen during chamber experiments.

Since average ambient temperatures measured during field burns were lower than those in the chamber, field OC measurements reported above may include additional condensed organic material. The OC/ EC ratio is negatively correlated with average ambient temperature measured during the field burns (Figure 4.3; three high OC background

samples- circled in Figure- were not subtracted from downwind measurements). This trend

is consistent with organic vapors condensing on to $PM_{2.5}$ during transport and might partly

explain the slightly higher field EFs for $PM_{2.5}$. It is unlikely that secondary OC formation

would be responsible for the trend in Figure 4.3, due to the short time between pollutant

generation and sampling.

Following the procedures outlined in Dhammapala et al. (2006b) the particulate

organic matter (POM)/ artifact corrected OC ratios during field experiments were 1.9 (KBG)

and 2.1±1.3 (wheat). This is close to the POM/ OC ratios from the chamber experiments

(1.5±0.1 for KBG and 1.5±0.2 for wheat).

4.4.3. Polycyclic aromatic hydrocarbons

Each gram of $PM_{2.5}$ emitted during wheat field burns consists of 0.2±0.2 mg PAHs

(solid phase PAHs include those with a molecular weight ≥ 202 g mol^{-1}- see Dhammapala et

al., 2006b). This is lower than the 0.7±0.1 mg g^{-1} measured during chamber experiments.

PAH content in $PM_{2.5}$ from KBG burns are similar when confidence intervals are taken into

account (field 0.2, chamber 0.3±0.1 mg g^{-1}). However the effects of plume dilution on phase

partitioning (Lipsky and Robinson, 2006) make comparisons of solid phase SVOCs less

straightforward.

To remove the effect of phase partitioning, the solid+ vapor phase PAH EFs were

compared in Figure 4.4. Relatively good agreement was observed for solid+ vapor phase

PAH EFs from wheat chamber burns at CEs >90%, however agreement was poor at lower

CEs. Overall the extrapolated solid+ vapor phase PAH EFs from chamber burns was 169%

of the field burns, for wheat. Individual PAHs in both phases from field and chamber

experiments were compared (by extrapolating EFs; data not shown) but no distinct trend was

seen. No data are shown for KBG because vapor phase PAH data were not collected for KBG burns.

4.4.4. Methoxyphenols

Species- specific solid phase MP/ $PM_{2.5}$ ratios are presented in Jimenez et al. (2006) and are not discussed here. To remove the effects of phase partitioning, the solid+ vapor phase MP EFs from field and chamber burns were compared (Figure 4.5). Though no vapor phase MP data are available for KBG, extrapolated solid+ vapor phase MP EFs from wheat chamber burns were 70% of the wheat field burns. The comparison of individual MPs in both phases from field and chamber experiments (by extrapolating EFs; data not shown) showed no distinct trend.

4.4.5. Comparison of ground and airborne data

Figures 4.6a and 4.6b show the comparison of EFs for CO and CH_4 as a function of CE, evaluated from ground and aircraft based samples, all collected during the wheat field burn on 2 August 2005. Aircraft based sampling captures the more buoyant sections of the plume (i.e. predominantly from the flaming phase with higher CEs and lower EFs). Ground measurements may be weighted toward less buoyant smoldering emissions (lower CEs, higher EFs) (Ward et al., 1992; Hurst et al., 1994). The ground-based sample with the highest CE (94.9%) was collected over the 20 minutes following field ignition. Five airborne grab samples taken over the same period had an average CE of 96.1%.

Based on data in Figure 4.6, it appears that ground based fixed-point measurements may not represent the CE of the whole plume, beginning from ignition to flameout. Yet since ground and airborne data appear to have similar EF- CE relationships, one data set

could be extrapolated to obtain a reasonable estimate of the other. The importance of reporting CEs alongside EFs is underscored.

A more accurate estimate of the plume- wide EFs is likely to involve combustion phase- specific EFs, weighted by the fraction of stubble mass consumed during the respective phase (Ward et al., 1982, Ward et al., 1992, Ortiz de Zarate et al., 2000). This exercise requires a knowledge of emissions and biomass consumption during each combustion phase, and cannot be attempted with the integrated measurements made here.

4.5.   CONCLUSIONS

It must be borne in mind that EFs from chamber burns are subject to uncertainties similar to those pertaining to field burns (Dhammapala et al., 2006a and 2006b). As a result, based on the propagation of errors, extrapolated chamber/ field EF ratios for PM$_{2.5}$, CO, EC and OC within 100±30%, and 100±45% for SVOCs, could still be considered within the bounds of experimental error.

Therefore chamber experiments conducted previously appear to provide reasonable representations of CO and PM$_{2.5}$ EF- CE relationships for wheat and KBG field burns, and particulate OC and solid+ vapor phase MPs from wheat field burns. The differences between PAHs in both phases from wheat field and chamber burns are in agreement for CEs> 90%, but are outside the aforementioned error limits at CEs< 90%. Though field EC EFs appear lower than the chamber, these differences may be partly caused by the TOT's inability to properly resolve the EC- OC split in chamber samples with high EC loadings. More KBG field burns are needed to facilitate better comparisons.

Utilizing more stubble than the 750g used in chamber burns might help better mimic flame structures, temperatures, intensities and burn rates seen during field burns. This may

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also improve the comparisons between chamber and field EFs. Average EFs evaluated from chamber experiments may be less biased toward either smoldering or flaming combustion than field measurements, since the chamber is well mixed. Chamber experiments might also be more amenable to calculating weighted emission factors, since the separation of combustion phases might be easier to accomplish than in the field.

4.6. ACKNOWLEDGEMENTS

4.7. REFERENCES

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4.8.   LIST OF FIGURES

Figure 4.1:   EFs vs. CE relationships determined in chamber and field burns for (a) CO and (b) $PM_{2.5}$. The trendlines and R^2 values superimposed on these charts were obtained from our previous chamber studies (Dhammapala et al., 2006a).

Figure 4.2:   (a) EC EFs vs. CE and (b) OC EFs vs. CE relationships determined in chamber and field burns. Circled OC data points had high backgrounds (see text). The trendlines and R^2 values superimposed on these charts were obtained from our previous chamber studies (Dhammapala et al., 2006b).

Figure 4.3:   OC/ EC ratio as a function of average ambient temperature measured during field burns. Circled data points have not been corrected for OC backgrounds (see text).

Figure 4.4:   Solid+ vapor phase PAH EF vs. CE relationship determined in chamber and field burns, for wheat stubble. The superimposed trendline and R^2 value was obtained from our previous chamber study (Dhammapala et al., 2006b).

Figure 4.5:   Solid+ vapor phase MP EF vs. CE relationship determined in chamber and field burns, for wheat stubble. The superimposed trendline and R^2 value was obtained from our previous chamber study (Dhammapala et al., 2006b).

Figure 4.6:   Comparison of EF- CE relationships from ground and aircraft based samples for (a) CO and (b) CH_4.
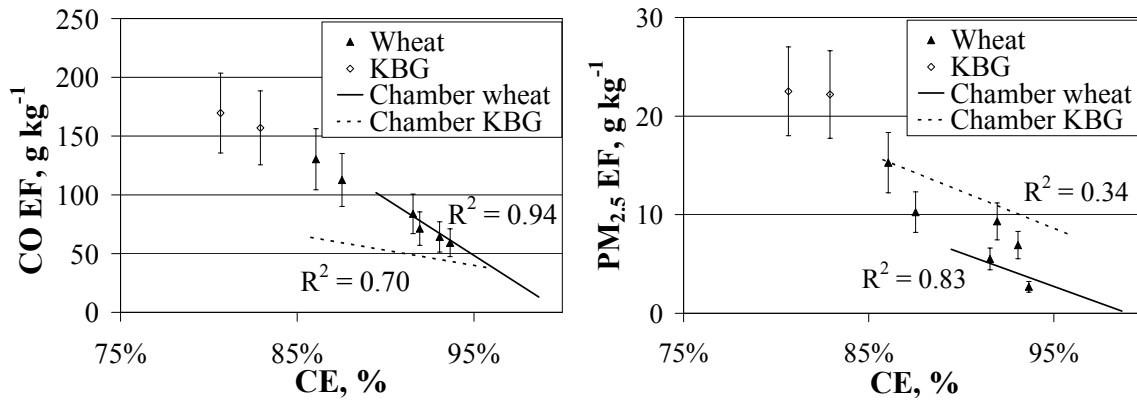
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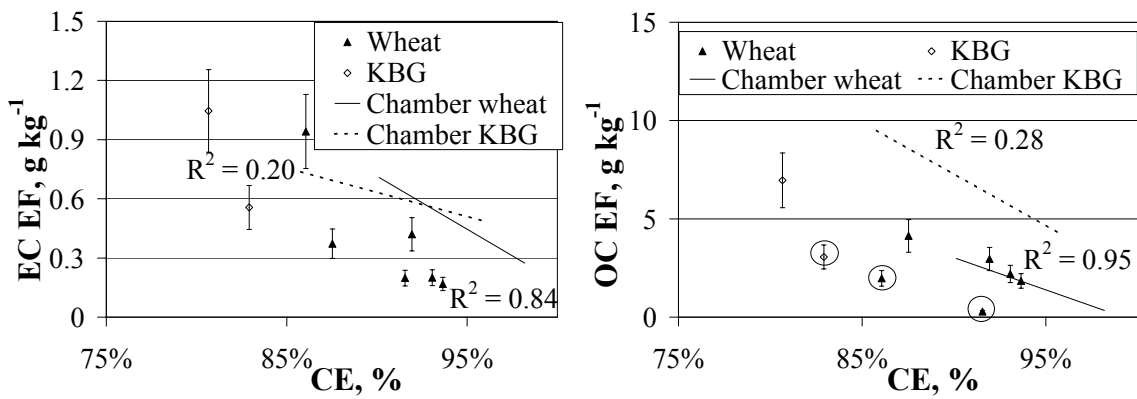
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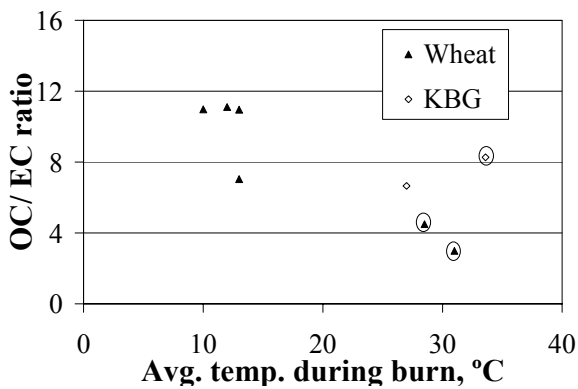
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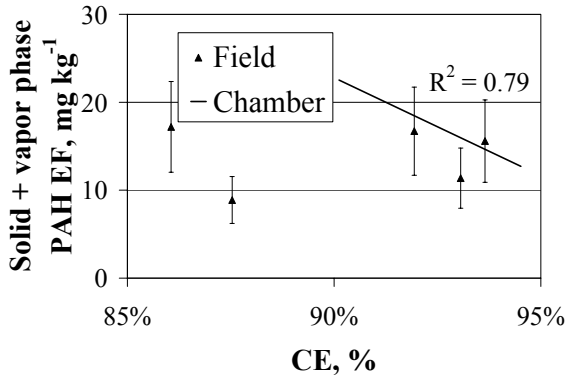
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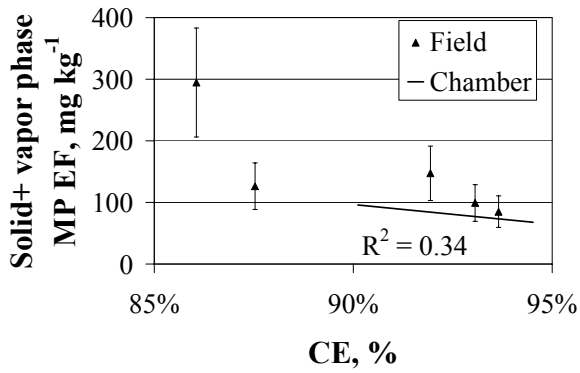
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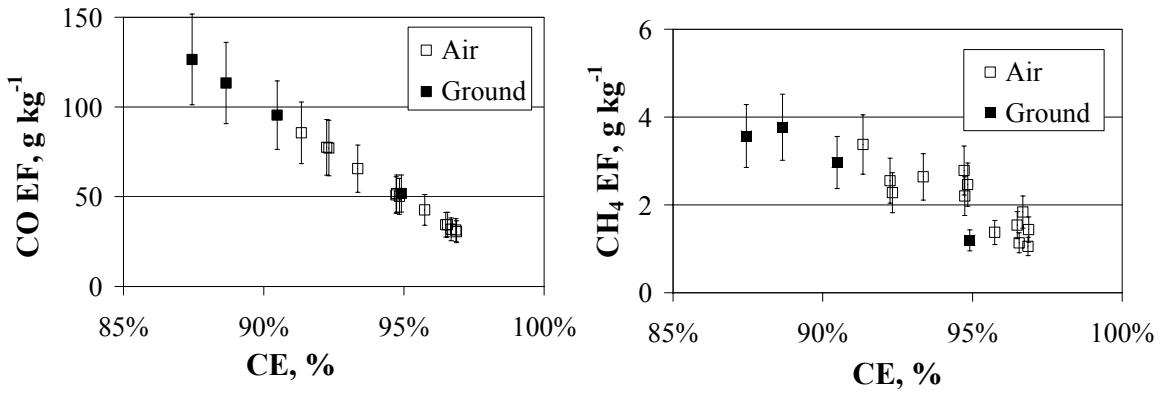
Figure 4.6.

Table 4.1:   Inventory of field burns conducted and samples collected

Date	Location	Upwind and downwind samples			
		CO_2, CO, CH_4	$PM_{2.5}$	QF and TQ	PUF
20 Aug and 8 Sep '04	Nez Perce County, ID (KBG)	4	1	1	-
29 Sep '04 and 18 Mar '05	Dayton, WA (wheat)	4^a	2^a	1^a	1^a
22 Mar '05	Colfax, WA (wheat)	4^a	2^a	1^a	1^a
23 Apr '05	Palouse, WA (2 wheat burns)	4^a	2^a	1^a	1^a
2 Aug '05	Connell, WA (wheat)	4^b	1^b	1^b	-

[a] Two sets of field duplicates were obtained

[b] Three sets of upwind samples were obtained. In addition 21 grab samples were collected from an aircraft by drawing smoke into syringes.

Table 4.2:   Precision of field duplicates

	Precision[a], %	# Duplicate samples
$PM_{2.5}$	9.9%	14
CO_2 (CO) [CH_4]	1.3% (3.5%) [2.2%]	12 each
EC (OC)	10.9% (7.2%)	2 each
PAH solid (vapor) phase[b]	19.5% (24.8%)	5 (2)
MP solid (vapor) phase[b]	26.6% (18.7%)	2 (2)

[a] Precision = absolute difference between two field duplicates/ mean

[b] Based on average of all individual SVOCs analyzed. The RSD of replicate laboratory analyses for PAHs was 14.2% (n=12) and 9.5% for MPs (n=4).

Table 4.3: Comparison of emission factors evaluated in chamber and field experiments

	$\left(\dfrac{\text{Chamber EFs extrapolated to field CEs}}{\text{Field EFs}}\right), \%$	
	Wheat	KBG[a]
CO	104±4	105, 110
PM$_{2.5}$	78±33	80, 87
EC	229±94	145, 83
OC	91±12[b]	176[b]
Solid+ vapor phase PAH	169±112	No vapor phase PAH data
Solid+ vapor phase MP	70±25	No vapor phase MP data

[a] Since n=2, EF ratios of both data points rather than their average, are shown.

[b] Samples with high backgrounds omitted (see text).

4.9. ELECTRONIC SUPPLEMENTARY MATERIAL

Table 4.A1: Concentrations of pollutants measured upwind and downwind of field burns.

		CO_2, ppm	CO, ppm	CH_4, ppm	$PM_{2.5}$, mg m^{-3}	OC, mg m^{-3}	EC, mg m^{-3}	ΣPAH, ng m^{-3} Solid phase	Vapor phase	ΣMP, ng m^{-3} Solid phase	Vapor phase
KBG, 20	Upwind	353	0.5	1.6	0.06	0.07[a]	0.00	111		237	
Aug '04	Downwind	391	7.3	2.2	1.03	0.20	0.02	221		756	
KBG, 8	Upwind	352	0.6	1.5	0.06	0.01	0.00	404		760	
Sep '04	Downwind	417	13.6	2.7	1.95	0.59	0.09	990		2637	
Wheat, 29	Upwind	346	0.6	1.6	0.04	0.19[a]	0.00	72	273	130	1976
Sep '04	Downwind	417	10.7	2.4	1.31	0.35	0.08	385	1383	9799	15829
Wheat, 18	Upwind	353	0.7	2.0	0.05	0.00	0.00	21	111	69	239
Mar '05	Downwind	459	13.6	3.0	1.52	0.54	0.03	165	1097	4969	11387
Wheat, 22	Upwind	356	0.8	1.9	0.09	0.00	0.00	23	233	86	300
Mar '05	Downwind	445	6.6	2.2	0.80	0.21	0.02	172	1246	2611	7916
Wheat, 23	Upwind	361	1.0	2.0	0.13	0.00	0.00	27	820	110	491
Apr '05	Downwind	774	31.3	4.5	4.25	1.34	0.19	662	7648	13230	53088
Wheat, 23	Upwind	361	1.0	2.0	0.13	0.00	0.00	27	820	110	491
Apr '05	Downwind	422	4.6	2.1	0.32	0.10	0.01	121	1773	1057	5206
Wheat, 2	Upwind	366	0.4	1.6	0.07	0.06[a]	0.02				
Aug '05	Downwind	478	10.1	2.1	0.71	0.07	0.05				

[a] Upwind OC concentrations are higher than $PM_{2.5}$ concentrations. Upwind OC from wheat burn of 2 Aug '05 accounts for 95% of $PM_{2.5}$. These samples are probably contaminated, and the average of other valid upwind OC concentrations was used instead.

5   EVALUATING OC ADSORPTION ON QUARTZ FILTERS AND COMPARING TWO METHODS FOR ESTIMATING ARTIFACT

PM$_{2.5}$ samplers with Quartz filters were deployed for sampling EC and OC. Though the adsorption of SVOCs on quartz filters causes the OC to be overestimated, this artifact may be accounted for by subtracting the OC collected on QbT or QbQ filters (Figure 5.1), from the OC on the Q filter (Mader et al., 2003; Pang et al., 2002; Turpin et al., 1994; Eatough et al., 1993). A list of EC and OC samples collected during chamber and field experiments is provided in Table 5.1.
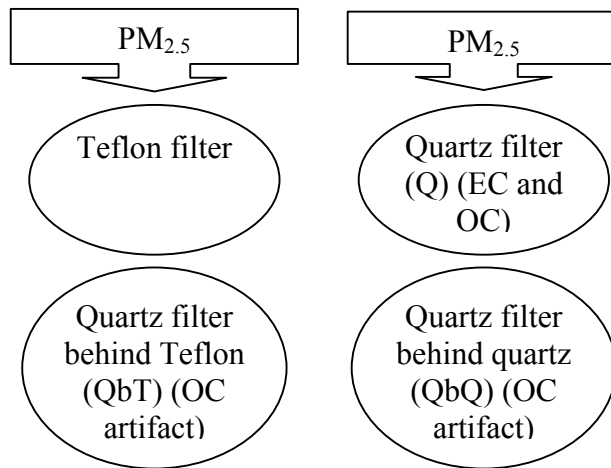
Figure 5.1:   Configuration of samplers used to trap EC and OC

Table 5.1:   Inventory of samples collected for EC and OC analysis, during field and chamber burns. Numbers in parentheses are the # of burns conducted.

	Chamber experiments			Field experiments[a]	
	May '01 (30)	Aug '03 (30)	July '04 (12)	Fall '04 (3)	Spring '05 (5)
Q	6	33	10	7	11
QbQ	4	33	-	-	-
QbT	1	29	10	7	11

[a] Includes samples collected upwind

5.1. ASSUMPTIONS OF THE DUAL FILTER METHOD

The QbQ and QbT methods assume the following:

- *The vapor adsorption capacities of both front and back quartz filters are equal*. Pang et al. (2002) point out that the surface functional groups, hydrophilicity, selectivity and sorptive capacity may vary between individual quartz filters and therefore the adsorption capacities of the front and back quartz filters may not be equal. Kirchstetter et al. (2001) showed that if quartz filters from the same batch were used, as was done here, the OC on back filters is more representative of the Q OC artifact.

- *SVOC evaporation off particles collected on the front (Teflon or quartz) filter is negligible and does not contribute substantially to the SVOCs observed on the back filter (i.e. negligible negative artifact).* Although some work shows little volatilization and subsequent adsorption of SVOCs (Pang et al., 2002; Mader et al., 2003), Subramanian et al. (2004) found that the QbT method over-estimated the adsorption artifact by 16%. This over-estimate was attributed to SVOCs evaporating from the Teflon filters and subsequently adsorbing on the QbT filter. However for the purpose of this research, it was assumed that the negative artifact has negligible effect on the overall OC concentrations. The scope of this discussion is limited to the net positive artifact.

- *The amount of vapor phase SVOCs adsorbed is the same for both the front and back quartz filters.* Some SVOCs are removed from the gaseous stream due to adsorption on Q filters. Hence a lower concentration of condensable SVOC reaches the QbQ filter. Therefore SVOC adsorbing on the QbQ filter may not equal that adsorbing on the Q filter, and the QbQ method may not be a very accurate measure of the positive artifact. However little SVOC adsorption is thought to occur on the Teflon filter upstream of a

QbT filter. Since the vapor phase SVOCs reaching both the Q and QbT filters are expected to be similar (Turpin et al., 1994), the QbT method may be a better representation of the adsorption artifact.

5.2. ANALYSIS OF EC AND OC

Rectangular 1.5 cm^2 punches of the quartz filters were analyzed for EC and OC with a Thermal Optical Transmittance (TOT) carbon analyzer (Sunset Labs Inc., Tigard, OR). The NIOSH reference method 5040 was used (NIOSH, 1999) with the following temperature program:

	Gas introduced	Temperature held for (seconds)	At temperature, ºC
	Helium	60	250
OC	Helium	60	500
analysis	Helium	60	630
	Helium	90	870
Cool oven, heater off for 30 seconds			
	He/ 2% O_2	10	500
	He/ 2% O_2	20	600
EC	He/ 2% O_2	20	670
Analysis	He/ 2% O_2	20	740
	He/ 2% O_2	20	810
	He/ 2% O_2	20	860
	He/ 2% O_2	120	940

Pyrolytically generated carbon (PC) is formed during TOT analysis and causes a lowering of the light transmittance through the filter. The introduction of O_2 results in the oxidation of any PC and this is accompanied by an increase in the transmissivity of the sample containing quartz filter. When all PC is removed, the transmittance of light through the sample returns to its initial value. This point in the thermogram is taken as the

demarcation of the OC- EC split. Carbon volatilized after this split is considered to be EC and the carbon evolved before this split is considered to be OC (NIOSH, 1999).

5.3. MAGNITUDE OF OC ARTIFACT

Figure 5.2 shows the magnitude of OC artifact evaluated with the QbT method, as a function of OC on the Q filter. The OC artifact can account for between 2- 57% of the Q OC in smoke samples (excluding ambient air samples). The artifact becomes less important at high Q OC levels. However these high OC concentrations are seldom encountered during field experiments, where concentrations are typically lower than in chamber burns.

At very low concentrations (mainly seen in ambient air sampled upwind of field burns) large fractions of the Q OC appeared to be artifact. However this could also be partly caused by analytical and/ or instrumental noise, which can substantially affect samples with low OC concentrations.
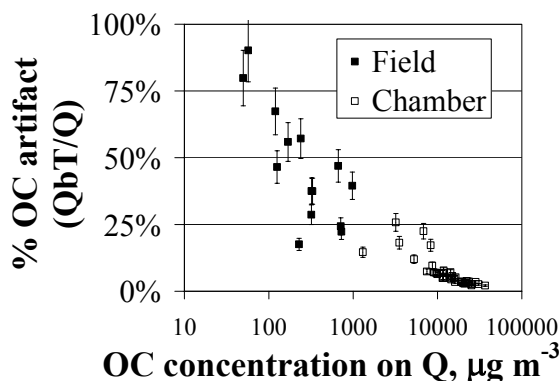
Figure 5.2: QbT- based artifacts evaluated during field and chamber burns

5.4. COMPARISON OF QBT AND QBQ ARTIFACTS

During the 2003 KBG chamber burns, the QbT artifact was 22.4±10.7% more than the QbQ artifact, at the average OC concentrations encountered during the KBG burns. However data presented in Figure 5.3 shows that QbT and QbQ artifacts appear to converge when higher OC levels were encountered. This is probably due to the high vapor phase OC

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concentrations present in the air not being affected much by condensation losses on the Q filter. Consequently the amount of OC reaching the QbQ filter is likely to be similar to the amount reaching the QbT filter. Another possible reason is that the frontal and backing quartz filters are saturated with condensable organics when high OC loadings are present. This would yield similar QbQ and QbT artifacts (Subramanian et al., 2004; Kirchstetter et al., 2001).
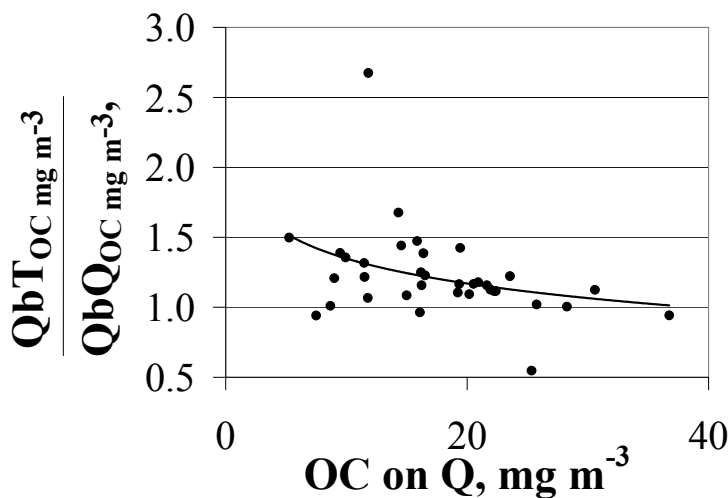
Figure 5.3:   Comparison of QbT and QbQ measured during KBG chamber burns of 2003

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6   EXTENSION OF RESEARCH: STUDYING THE EFFECTS OF SMOKE AGING

As smoke plumes are transported downwind of the source, several secondary processes including gas-to-particle conversion, coagulation and sedimentation of particles, alteration of solid-vapor equilibrium and photochemical reactions are known to occur (Seinfeld and Pandis, 1997; Turpin et al., 1994; Hobbs et al., 2003; Radke et al., 1995; Lipsky and Robinson, 2006; Kamens et al., 1988). Certain secondary atmospheric processes may degrade specific SVOCs during transport. These include solid phase PAH- O_3 reactions, and vapor phase PAH- OH radical reactions, both of which result in PAH lifetimes of less than an hour (rate constants from Pöschl et al., 2001; Alebić- Juretić et al., 1990; Calvert et al., 2002). Additionally, PAHs have been shown to react with methoxyphenols (Kjällstrand and Petersson, 2001; McDow et al., 1994). Therefore emission factors reported in the previous chapters are valid at the point of emission only.

Transformational phenomena occurring during smoke aging need to be accounted for in dispersion models in order to accurately predict the impacts of burning, pave the way for improved burn management, and enact appropriate health protection laws. This chapter discusses potential experiments to study the effects of smoke aging, and outlines some of the preliminary research conducted in this regard. Since smoke from agricultural burns typically impacts a limited geographic area, plumes need to be tracked and studied over a period of 5-6 hours.

6.1.   SMOKE AGING: SOME IDEAS FOR A CHAMBER EXPERIMENT

The exhaust gases from a test burn chamber will be diverted to a transparent Teflon chamber ($> 20m^3$ preferred) located outdoors. While filling with smoke, the Teflon chamber

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is covered with black tarpaulin to defer the onset of any photochemical processes. To mimic atmospheric processes, the smoke is diluted continuously with ambient air, at rates reflective of atmospheric dilution. The smoke mixes with dilution air, but mechanical agitation is not desirable as it enhances particle losses to chamber walls. Therefore dilution air is introduced into the chamber from several locations simultaneously.

The impact of secondary processes on $PM_{2.5}$ and SVOC concentrations is monitored by analyzing grab samples, drawn at 30-minute intervals. The difference between the initial pollutant concentration corrected for dilution, and the concentration in aged smoke is the net effect of the secondary processes. During sampling, the Teflon chamber is covered with black tarpaulin, and the flow of dilution air stopped. Air is sampled over no more than 10 minutes (requires a pump capable of at least 20 L min^{-1}). Samples are drawn from the center of the chamber, to minimize wall effects.

An Aerodynamic Particle Sizer (TSI Inc., St Paul, MN) is deployed to monitor the particle size and number distribution continuously. This will also help ascertain the extent of shift in particle size distribution as a function of smoke age. Continuously diluting air in the chamber will also reduce particle number concentration and therefore wall losses. Monitoring SVOC concentrations on Teflon filters and PUFs will help determine how the solid-vapor partitioning of SVOCs is altered as a function of aging time.

Experiments should be repeated at different humidities, dilution rates, solar radiation intensities and temperatures. Figure 6.1 summarizes the experimental setup.
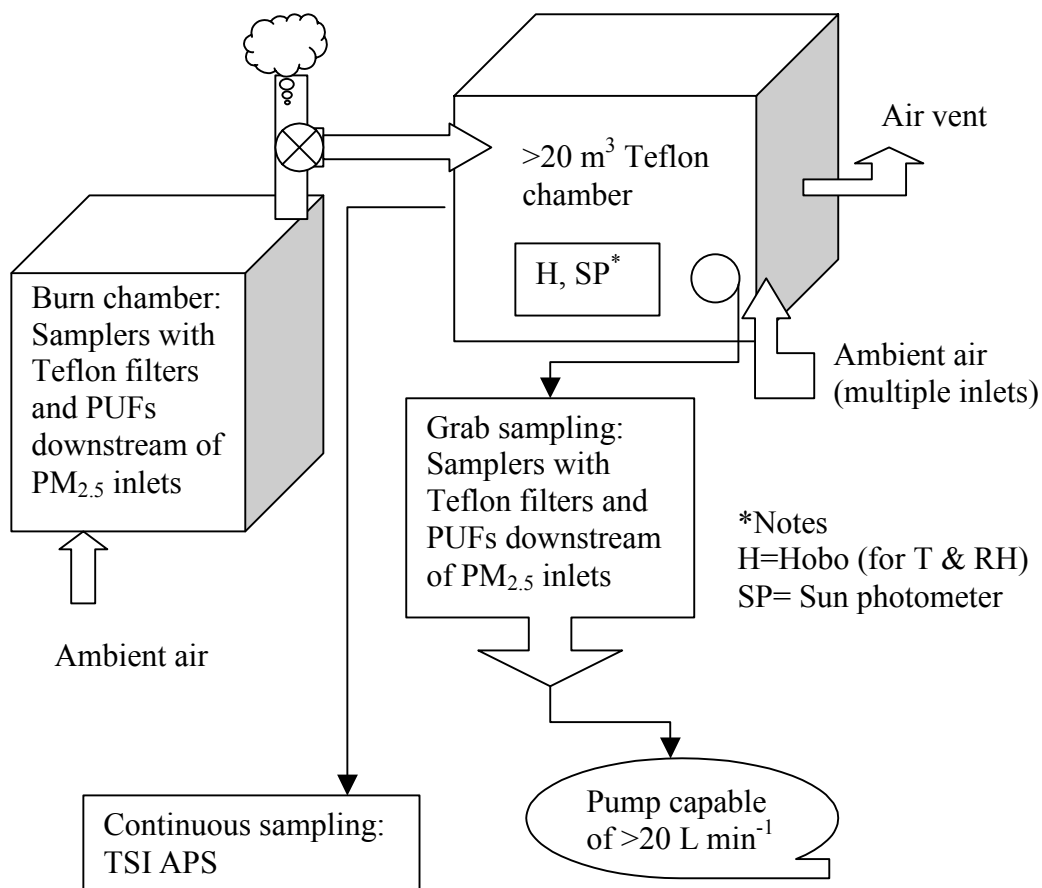
Figure 6.1:   Schematic of a chamber experiment to study effects of smoke aging.

6.2.   SMOKE AGING: SOME IDEAS FOR A FIELD EXPERIMENT

Due to the many variables affecting secondary processes, it is more practical to conduct controlled chamber scale experiments and subsequently use field measurements to verify their applicability. Plume tracking and airborne sampling are probably the most challenging tasks in the field. Multiple plumes may emanate from a single field burn and it is necessary to ensure that the same plume is tracked and studied.

A tracer molecule (SF_6) can be used to account for atmospheric dilution. To mimic the release of pollutants by the fire, a line of several balloons, each filled with 1000 ppm SF_6 can be moored in the path of the advancing fire (Lamb, personal communication). The ratio

of SF_6 concentrations measured during the fire at any two locations, is the extent of atmospheric dilution between those two points.

An instantaneous release of a visual tracer (colored smoke from a canister, with a known chemical fingerprint) is needed to track the plume at the initial stages until its maximum height is reached. This release must coincide in time and space with the SF_6 release. At the maximum plume height, a visual marker of neutral buoyancy is released from the plane, in order to track the plume further downwind.

Test burns must be conducted when moderate winds are present and strong inversions are absent. Ground-based measurements of $PM_{2.5}$ and solid and vapor phase SVOCs can be made as close as possible to the source. Further downwind, samples can be collected with the use of a cherry picker. After the maximum plume rise has been attained sampling can be conducted on board a light aircraft (see Figure 6.2).

Obtaining size-selective particulate matter samples from an aircraft requires an isokinetic sampling inlet (discussed in Appendix B). Total suspended particulate matter (TSP) may be measured instead, with stationary samplers (ground and cherry picker based measurements) configured to provide a TSP/ $PM_{2.5}$ ratio. Airborne measurements can then be scaled to obtain the $PM_{2.5}$ concentration. Solid and vapor phase SVOCs, particle size distribution, temperature, humidity and solar intensity should be monitored.

As with the chamber study, the net effect of the secondary processes is the difference between the initial pollutant concentration (i.e. ground based measurements) corrected for dilution, and the concentration measured downwind.

Figure 6.2: Proposed field experiment to study the effects of smoke aging (cliparts from http://www.fotosearch.com).

6.3. PAH DEGRADATION CAUSED BY OZONE

O_3 is formed photochemically in plumes from chamber and field burns. Several authors report that O_3 reacts with PAH samples collected on filter substrates (Pöschl et al., 2001; Peltonen and Kuljukka, 1995; Finlayson- Pitts and Pitts, 2000; Van Vaeck and Cauwenberghe, 1984; Alebić- Juretić et al., 1990; Schauer et al., 2003; Fraser et al., 1998), thereby underestimating PAH concentrations. NO_2 is not thought to significantly degrade PAHs (Schauer et al., 2003; Peltonen and Kuljukka, 1995; Finlayson- Pitts and Pitts, 2000). H_2O_2 is unlikely to remove much PAHs, since ambient H_2O_2 concentrations are typically a few ppb (Seinfeld and Pandis, 1997). A detailed literature survey on O_3 induced degradation of PAHs is presented in Appendix C.

When studying the aging of fresh smoke, PAH degradation rates higher than those reported in the studies cited in Appendix C may be expected, on account of the following:

- PAHs on freshly emitted smoke particles may degrade faster than those on aged or partially aged plumes, since the outermost layer on fresh particles is likely to contain PAHs that are yet to undergo photochemical transformations.

- Heterogeneous chemistry is likely to occur on smoke particles that contain a liquid organic layer (see section on "Effects of humidity" in Appendix C). The PAH decay could be faster than reported in the experiments involving dry particles.

- Compared to high volume samplers, the low volume samplers utilized in our experiments permit the topmost layer of PAHs already deposited on the Teflon filters, to be in contact with O_3 for longer. The linear velocity of air through the low volume samplers is 5 cm s^{-1}, whereas Tsapakis and Stephanou (2003) operated their samplers at 75 cm s^{-1}.

To avoid a negative artifact when sampling PAHs, it is necessary to remove atmospheric oxidants from the air stream being sampled. This is typically accomplished with a denuder placed upstream of the PAH sampling media.

6.3.1. Development of the denuder

Denuders used in the Versatile Air Pollution Sampler (VAPS) system (22 cm long, 1.9 cm ID, 4 concentric etched glass tubes), were washed several times in de-ionized water and methanol and sonicated several times to remove any contamination. After thorough drying using a gentle stream of purified air, they were coated with a saturated KI solution. The gap between glass rings is 0.1 cm. Laminar flows are expected at an air flowrate of 5 L/ min, and the overall mass transfer coefficient was 2.7 cm s^{-1}. The residence time of air in the denuder (0.36 sec) is sufficient for O_3 diffusion to the denuder walls. The O_3- KI reaction rate is sufficiently fast (Perry and Young, 1977) for near- quantitative removal of O_3. The additional pressure drop in the PAH sampling system, caused by the addition of the denuder is negligible.

Though glycerol has often been included to increase the "stickiness" of the coating solution, this has been reported to cause a positive artifact in the $PM_{2.5}$ mass (Finn et al., 2001) and was not used here. During testing it was seen that KI crystals were deposited on the Teflon filter downstream of the denuder. Therefore a 5% (w/w) KI solution was used instead, and the O_3 removal efficiency was assessed by challenging the denuder with a stream of 120 ppb O_3 (from an O_3 generator) overnight. No detectable amounts of O_3 [measured with a TECO O_3 analyzer, model 49 (Thermo Electron Corp., MA)] were seen downstream of the denuder. No additional mass (KI crystals) was deposited on the Teflon filter downstream.

6.3.2. Testing O_3 denuder during chamber burns

Denuders coated with a solution of 5% KI were fitted directly on top of the $PM_{2.5}$ sampling inlets (Figure 6.3). The PAHs and $PM_{2.5}$ sampled on Teflon filters and PUFs downstream of the denuder were compared with corresponding measurements made on undenuded samplers (Table 6.1). Since no O_3 was observed during chamber burns (see Chapter 3) this comparison serves to evaluate the net effect caused by the physical presence of the denuder.

Figure 6.3: O_3 denuder on $PM_{2.5}$ sampler.

Table 6.1:   PM$_{2.5}$ and PAHs in denuded samples: comparison with undenuded samples.

	Denuded/ undenuded	Paired t-test to compare denuded and undenuded samples
PM$_{2.5}$	1.03	$t_{0.05,4}$=1.23; P=0.29
Solid phase PAHs[a]	0.93	$t_{0.05,2}$=1.80; P=0.21
Vapor phase PAHs[a]	1.07	$t_{0.05,3}$=1.72; P=0.18

[a] Based on sum of all individual PAHs analyzed

Data in Table 6.1 suggest that the denuder does not appear to significantly alter the PAH or PM$_{2.5}$ concentrations reaching the sampling media. Pollutant losses to the denuder walls and potential KI crystal deposits on Teflon filters appear to be small. Pollutant losses to denuder walls can be accounted for with the undenuded sampler operated in parallel (equation 1):

$$\text{PAH corrected for denuder wall losses} = \left(\frac{\text{PAH}}{\text{PM}_{2.5}} \right)_{\text{denuded}} \times \text{PM}_{2.5 \text{ (undenuded)}} \qquad (1)$$

It was concluded that this KI-based oxidant denuder is suitable for use in smoke aging experiments, such as those described in the preceding sections.

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7   SYNOPSIS

This work presents some of the first measurements of emission factors of EC, OC, LG and SVOCs from KBG stubble burning, and some of the first field measurements of the same pollutants from wheat stubble burning. To recapitulate, the main objectives of this research were to:

- Evaluate emission factors of CO, hydrocarbons, $PM_{2.5}$, EC, OC, LG, PAHs and MPs from wheat and KBG burning as a function of CE, with the aid of chamber- scale burn experiments.

- Compare the emission factors evaluated in the chamber with those determined from field studies.

7.1.   EMISSION FACTORS FROM CHAMBER EXPERIMENTS

The average EFs of each pollutant for wheat and KBG, determined from chamber experiments are summarized in Table 7.1. Due to the potential for secondary atmospheric processes, these EFs are valid at the point of emission only.

Table 7.1:   Summary of EFs evaluated from chamber burns

	Wheat	KBG
$PM_{2.5}$, g kg^{-1}	3.0±0.6 (CE 95±0.8%)	12±1.4 (CE 90±1.0%)
CO, g kg^{-1}	53±8.0 (CE 95±0.8%)	52±3.3 (CE 90±1.0%)
THC, g kg^{-1}	2.2±0.4 (CE 95±0.8%)	11±1.3 (CE 90±1.0%)
EC, g kg^{-1}	0.35±0.16 (CE 96±2.1%)	0.63±0.056 (CE 90±1.0%)
OC^a, g kg^{-1}	1.9±1.1 (CE 94±3.2%)	6.9±0.85 (CE 90±1.0%)
ΣPAHs^b, mg kg^{-1}	17±8.2 (CE 93±3.3%)	21±15 (CE 85±4.2%)
ΣMPs^b, mg kg^{-1}	79±36 (CE 93±3.3%)	35±24 (CE 85±4.2%)
LG, mg kg^{-1}	150±130 (CE 92±2.7%)	350±510 (CE 86±9.8%)

[a] Corrected for the positive artifact caused by vapor adsorption onto quartz filters

[b] Sum of 19 species in solid and vapor phases

EFs in Table 7.1 are in reasonable agreement with other similar data reported in literature, although KBG EFs are hard to compare due to the scarcity of published data. MP EFs appear dependent on the stubble type as well as on CE, and are lower than the EFs for hard and softwoods reported in literature, possibly due to lower lignin content in wheat and KBG.

Table 7.2 compares $PM_{2.5}$, EC and OC EFs evaluated during the wheat burns of 2001, against parallel measurements made with a dilution sampler (Hays et al., 2005). The EC data is in agreement as expected, since EC does not typically undergo secondary effects.

The OC concentrations measured by the dilution sampler ranged from 60-260 $\mu g\ m^{-3}$ (Hays, personal communication), and were not corrected for adsorption artifacts. According to Figure 5.1, OC at these concentrations could consist of approximately 50% artifact. As the plume ages, particulate OC content can increase due to vapor phase OC condensation, and secondary OC formation (the latter may not occur in large amounts given the absence of photochemistry inside the dilution sampler, as well as the short duration). Re-adjustment of phase distributions during dilution can cause OC to volatilize off particles, in order to remain in equilibrium with the diminishing vapor phase concentration (Lipsky and Robinson, 2006). Although the OC data in Table 7.2 suggest that artifacts and processes occurring during dilution approximately offset each other, it is not possible to make any generalized conclusions.

Since OC makes up a large fraction of $PM_{2.5}$, considering the fact that OC EFs are hardly affected by dilution, the higher $PM_{2.5}$ EFs in the dilution sampler suggests that some inorganic mass may be added to the $PM_{2.5}$, possibly through gas to particle formation. It is

also possible that some OC condensing onto existing particles contains heavier oxygenated species, which are not lost in large amounts during off- gassing.

Table 7.2:   Comparison of dilution sampler and chamber measurements, all collected during wheat burns of 2001.

	Chamber based samples	Dilution sampler (Hays et al., 2005)
EC EF, g kg^{-1}	0.47±0.079[a]	0.52±0.00
OC EF, g kg^{-1}	1.37±0.25[a]	1.23±0.03
PM$_{2.5}$ EF, g kg^{-1}	3.0±0.6	4.71±0.04

[a] Extrapolated from all wheat data, to average CEs of 2001 wheat burns. Uncertainties are standard regression errors.

When conducting chamber experiments, it is necessary to orient the stubble as found in the field, since stubble orientation was seen to affect EFs. The compact-ness of KBG straw implies less contact with ambient air compared to the more spaced out, hollow, wheat straw. Compared to wheat, a larger KBG stubble mass fraction was consumed during the slow propagating, low CE smoldering phase, which also dissipates less heat than flaming combustion. These factors could partly explain the observed differences between CEs, ΔTs and burn rates of wheat and KBG fires.

During chamber burns, a separate method for evaluating EFs [the EF(carbon) method] was tested and found to be a viable tool for use during field experiments, and was subsequently employed during field burns.

7.2.   COMPARISON OF FIELD AND CHAMBER EXPERIMENTS

Table 7.3 provides a comparison between EFs evaluated with chamber and field burns. The chamber EFs were extrapolated to the CEs encountered in the field, and compared with the EFs evaluated in the latter.

Table 7.3:   Comparison of EFs evaluated in the field against those evaluated with the aid of chamber burns

	$\left(\dfrac{\text{Chamber EFs extrapolated to field CEs}}{\text{Field EFs}} \right), \%$		Expected chamber/ field EF ratio[b]
	Wheat	KBG[a]	
CO	104±4	105, 110	100±30%
PM$_{2.5}$	78±33	80, 87	100±30%
EC	229±94	145, 83	100±30%
OC	91±12[c]	176[c]	100±30%
Solid+ vapor phase PAH	169±112	[d]	100±45%
Solid+ vapor phase MP	70±25	[d]	100±45%

[a] Only 2 field burns were conducted; EF ratios of both data points rather than their average, are shown.

[b] Uncertainties based on error propagation

[c] Samples with high backgrounds omitted (see Section 4.4.2).

[d] No vapor phase data available

By comparing the extrapolated EF ratios against expected EF ratios (Table 7.3) it can be seen that chamber experiments provide a reasonable representation of CO and PM$_{2.5}$ EF-CE relationships for wheat and KBG field burns, and particulate OC and solid+ vapor phase MPs from wheat field burns. The differences between PAHs in both phases from wheat field and chamber burns are outside the aforementioned error limits, but are in agreement for CEs> 90%. It is possible that variables besides CE are responsible for some of the observed differences. Differences between field and chamber EC EFs may be partly caused by the TOT incorrectly assigning the EC- OC split in chamber samples with high EC loadings.

More KBG field burns are needed to facilitate better comparisons. Utilizing more stubble than the 750g used in chamber burns might help better mimic flame structures, temperatures, intensities and burn rates seen during field burns. This may improve the comparisons between chamber and field EFs.

7.3. WEIGHTED EMISSION FACTORS: SEPARATION OF COMBUSTION PHASES

Combustion phase- specific EFs, when weighted by the fractional mass burned during the respective phases, are likely to provide a more realistic picture of overall EFs. The separation of phases is more easily accomplished during chamber experiments, since the stubble mass burn rate is continuously recorded.

When most volatile substances have been released from the near-surface region of the fuel, flaming combustion tapers off and smoldering combustion begins (Andreae and Merlet, 2001), although there is a short period during which both flaming and smoldering occur simultaneously. The flaming phase has sometimes been pre-determined to occur over the first 6 to 10 minutes of the fire (Ward et al., 1992; Air Sciences, 2003), and all smoke samples collected after this period were assumed to contain products of smoldering combustion only.

It is thought that the criteria listed below could be used to obtain a more accurate estimate of the length of the flaming phase. The time at which each criterion was met, was noted from the data logs of the continuous emission monitors.

- Flame extinguished

- Maximum CE

- Peak burn rate

- Peak rate of change of CO concentrations, with respect to time

The real-time profiles of CO_2 and $PM_{2.5}$ concentrations, CE, burn rate and d[CO]/dt are shown in Figure 7.1. Each of the above criteria were met within the space of 45 seconds.
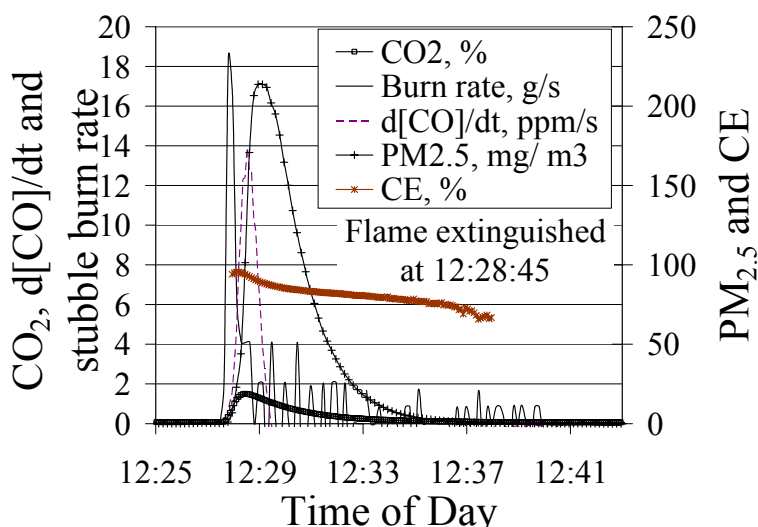
Figure 7.1:   Time series of pertinent parameters measured during a typical chamber burn.

The following procedures were then observed, to estimate weighted EFs:

1. The average CE and stubble mass fraction burned during the flaming phase, were calculated from the start of the fire until the time at which each of the above criteria were fulfilled (this yields four possible CEs and mass fractions, for each burn experiment).

2. Smoldering phase CE and mass burned were estimated by averaging the remainder of the respective time series.

3. Weighted $CE = \sum_{i=Fla\min g}^{Smoldering} \left(CE_i \times \text{mass fraction burned}_i \right)$

4. With the weighted CE known, the EF- CE relationships in the preceding chapters can be used to read off the weighted EFs.

For each burn, the relative standard deviation (RSD) of the four flaming phase CEs and mass fractions, were calculated. The corresponding RSDs from all burns averaged 0.2% and 8%, respectively. This implies that the estimation of flaming phase CEs and mass fraction burned was not strongly dependent on the choice of criteria employed to identify the end of the flaming phase.

Figure 7.2 shows that the flaming phase mass fraction (range 63-90%) was positively correlated with flaming phase CEs (range 91-99%). Flaming combustion consumed 72±9% and 83±10% of KBG and wheat stubble mass, respectively. This is in reasonable agreement with the assumed value of 90% for wheat (Ortiz de Zarate et al., 2000). Ward et al. (1992) reported a value of 36% for forest fires, although those fires were characterized by lower CEs.

Figure 7.2:   Relationship between CE and stubble mass fraction burned, during the flaming phase.
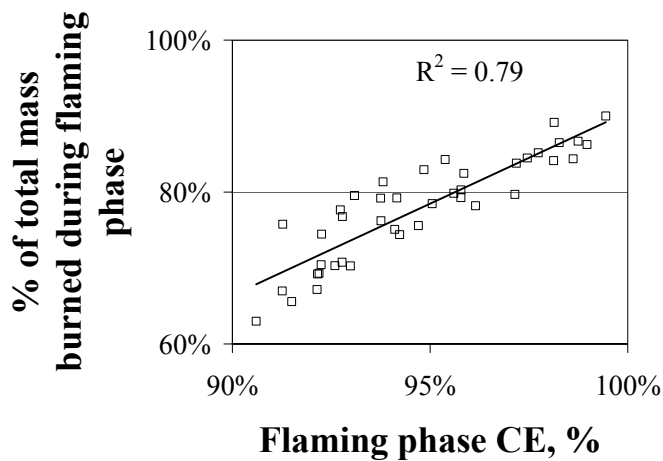
Smoldering phase CEs ranged from 79-91%. The average RSD of weighted CE calculated using each of the above-mentioned criteria, was 0.6%. It was observed that

weighted CEs for the chamber data were very consistent with overall CEs evaluated from integrated samples.

The average CEs of ground- based field samples (assumed to be smoldering phase) and aircraft samples (assumed to be flaming phase) were used in conjunction with the flaming phase mass fraction, to estimate the average weighted CE of field burns. In the absence of aircraft measurements during KBG burns, the CE of the KBG flaming phase was extrapolated from the wheat/ KBG CE ratio from ground data, and the CE from airborne measurements of wheat. The weighted CEs of wheat (94%) and KBG (85%) field burns, along with the outputs of linear regression applied to chamber EF- CE relationships (Figures 2.1- 2.3, 3.2- 3.5), were then used to calculate weighted EFs from wheat and KBG burns (Table 7.4), for subsequent use in air quality models.

Table 7.4:   Weighted EFs for use in dispersion models (uncertainties are standardized errors of regression).

	Wheat (CE 94%)	KBG (CE 85%)
$PM_{2.5}$, g kg^{-1}	3.4±0.93	16±3.2
CO, g kg^{-1}	57±7.4	148±7.4[a]
THC, g kg^{-1}	2.4±0.96	16±2.3
EC, g kg^{-1}	0.50±0.079	0.76±0.15
OC, g kg^{-1}	1.7±0.25	10±2.6
ΣPAHs, mg kg^{-1}	14±3.0	22±13
ΣMPs, mg kg^{-1}	71±23	36±21
LG, mg kg^{-1}	130±96	410±29

[a] Due to the unexpected CO EF- CE relationship in the KBG chamber burns, this EF was calculated by extrapolating the trendline for wheat chamber burns.

7.4. CONCLUSION

Since EFs are smoke management tools, dispersion models employed within forecast systems (such as the ClearSky project -http://www.clearsky.wsu.edu) could utilize EFs and assist authorities determine the advisability of agricultural burning. Since EC and CO do not typically undergo secondary atmospheric processes, their EFs can be fed into dispersion models with the aim of reconciling model outputs with downwind measurements. In addition to EFs, an understanding of secondary processes undergone by $PM_{2.5}$ and PAHs is necessary for predicting human exposure to these pollutants at downwind locations. The laboratory and field experiments outlined in Chapter 6 could be employed to quantify some of the main secondary processes occurring over a few hours.

The LG and MP EFs presented here are useful for mapping source signatures, which are required for receptor modeling. Emission inventories can also be compiled using EFs evaluated here. The adsorption of SVOCs onto quartz filters can cause a substantial overestimation of OC measurements (depending on OC concentrations in the smoke plume), if left uncorrected.

Comparison with county- wide emissions suggests that smoke from agricultural burns can make up a sizeable fraction of localized emissions. Since EFs of pollutants measured here are inversely correlated with CE, identifying methods of increasing the CEs of burns would help reduce the impacts of agricultural field burning.

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APPENDIX A: ADDITIONAL RESULTS FROM CHAMBER BURNS

Table A.1:   Flows and residence time distribution measured with the SF_6 tracer

experiment

	Volumetric flowrate of dilution air, $m^3 min^{-1}$	Expected residence time of SF_6 in chamber, min	Residence time (±1 SD) calculated from F- curve, min
May 2001 and first 11 burns of August 2003	9.6	2.2	2.0±1.1
August 2001	7.2*	N/A	
Last 19 burns of August 2003	14.0	1.4	1.5±0.8

* It was not possible to set the corresponding fan speed. This flow was calculated as 75% of

the flowrate used in May 2001.
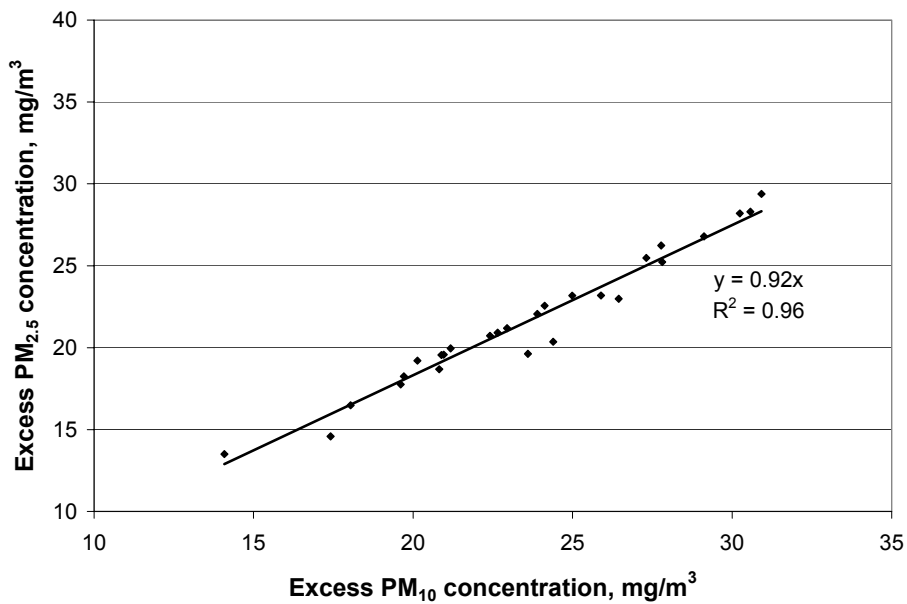
Figure A.1:   Comparison of PM_{10} against $PM_{2.5}$ in August 2001

A.1. RETENTION EFFICIENCY TESTS

Retention efficiencies (i.e. a measure of sampling and storage losses) were evaluated by spiking typical samples with deuterated PAH and MP mixtures prior to sampling, and evaluating the fractional deuterated SVOC mass recovered. 6 PUFs and 4 Teflon filters were spiked with a mixture of 5 d-PAHs, and 4 PUFs were spiked with a mixture of 13 d-MPs. The deuterated SVOC mass measured is a function of the spiked mass, sampling, storage and analytical losses. We corrected for losses during analysis by normalizing by average extraction efficiencies of all samples (see Figures A.5a and A.5b). The results of the retention efficiency tests are shown in Figures A.2 and A.3. Numbers in parentheses are PAH molecular weights (MW). Error bars are ±1 SD (propagated).
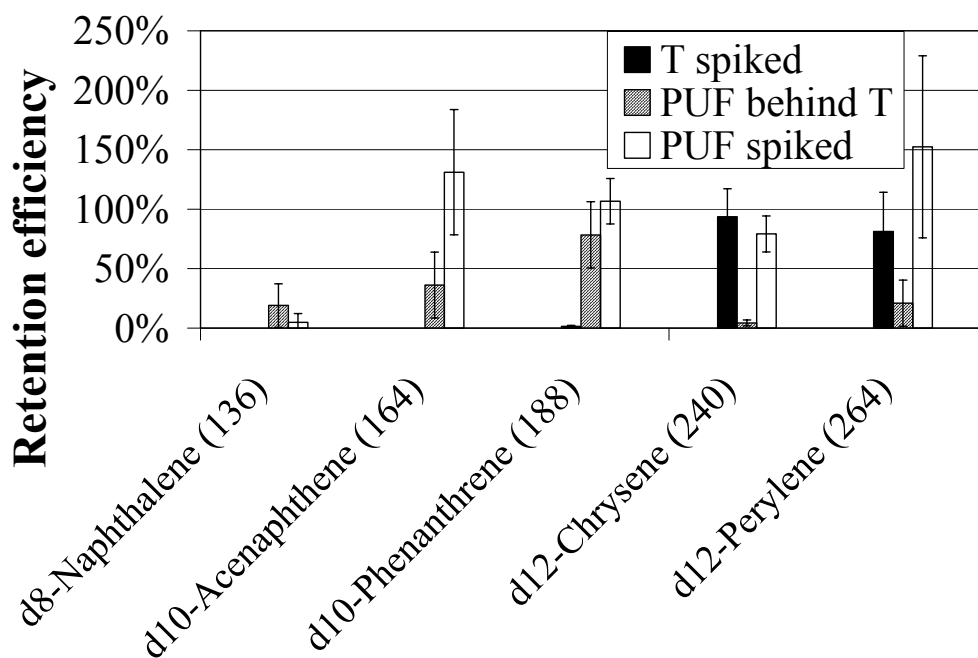
Figure A.2:   Results of PAH retention efficiency tests.

Average retention efficiencies are 87±28% (Teflon, MW ≥202 g mol^{-1} only) and 117±41% (spiked PUF, excluding d8-naphthalene). Most PAHs show near- quantitative retention on PUFs, except d8-naphthalene, which is not retained well in either medium and

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is not discussed further. Lighter, more volatile d-PAHs are poorly retained on the Teflon filters and tend to migrate to the PUFs located downstream, whereas heavier PAHs remained mostly in the solid phase. Directly spiked PUFs retain d10-acenaphthene well, although Teflon filters + downstream PUFs show lower-than- expected retention efficiencies. This may be due to some volatilization off Teflon filters during the few minutes between spiking and commencement of sampling.

Data in Figure A.2 are consistent with the findings of Schauer et al. (2001), who reported only small amounts of PAHs with up to 3 benzene rings in the solid phase (except retene). For this reason references to "solid phase PAHs" refer to with MW ≥ 202 g mol^{-1}. References to "solid + vapor phase PAHs" imply the sum of all measured species collected on Teflon filters and PUFs, except naphthalene.

Teflon filters were not spiked with d-MPs since most of these are expected to predominate in the vapor phase (Schauer et al., 2001). MP retention efficiencies on the PUFs are shown in Figure A.3.
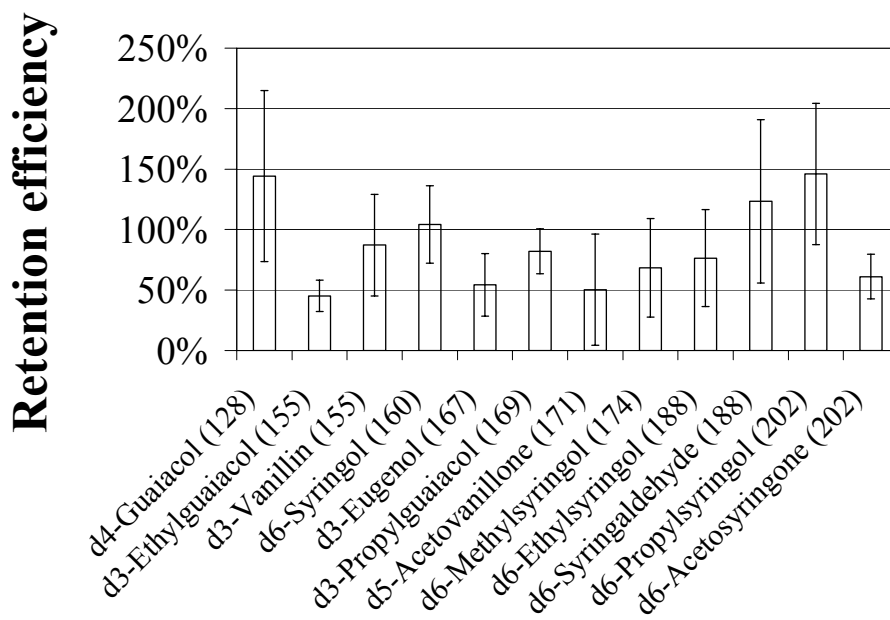
Figure A.3: MP retention efficiencies on PUFs.

The average MP retention on PUFs is 81±39%. PUFs appear to retain MPs with reasonable efficiencies, although slightly lower retention was observed for d3-ethylguaiacol, d3-eugenol and d6-acetosyringone. Throughout the rest of this document, "MP EFs" refer to the sum of solid and vapor phases, unless otherwise stated.

A.2.   EXTRACTION EFFICIENCY TESTS

For determining the extraction efficiencies of samples analyzed at EWU, 4 each of blank Teflon filters and PUFs were spiked with 50 µL of the 1000 µg mL^{-1} semivolatile calibration standards mixture. They were analyzed for PAHs after air-drying for 30 mins. The results are shown in Figure A.4. Error bars are ± 1 SD.
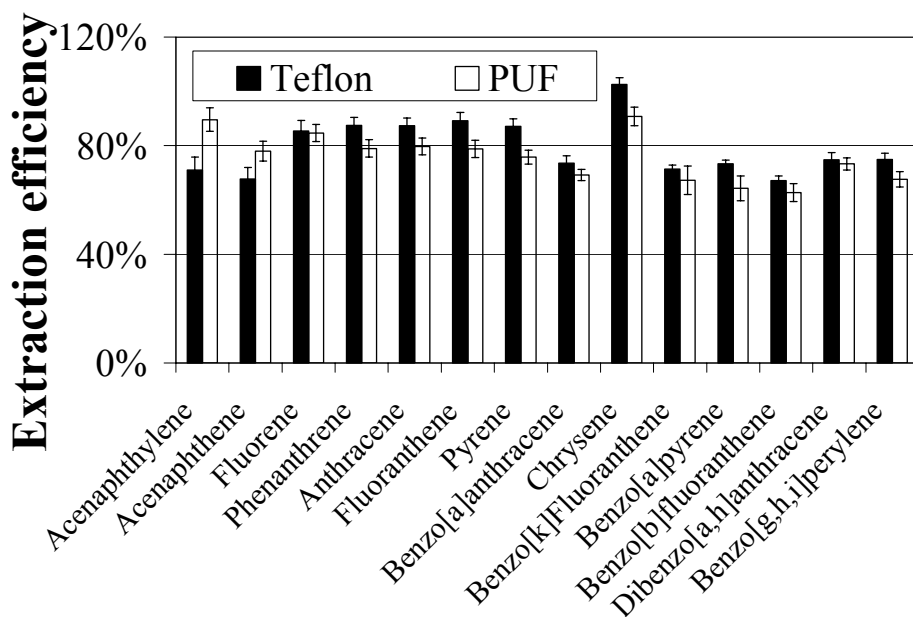
Figure A.4: Results of EWU extraction efficiency tests.

Average PAH extraction efficiencies of EWU samples (69±3% for Teflon and 77±4% for PUFs) appear reasonable and consistent. The extraction efficiencies of UW samples were determined by (i) spiking 20 Teflon and 20 PUF samples with 20 µL of a 2 µg

mL^{-1} d-PAH standards mixture, and (ii) spiking 10 Teflon and 10 PUF samples with 20 μL

of a 2 μg mL^{-1} d-MP standards mixture, and assessing the fractional deuterated SVOC mass

detected by the GC/MS. Extraction efficiencies for PAHs and MPs are shown in Figures

A.5a and A.5b respectively. Error bars are ±1 SD.

Figure A.5:   Results of UW extraction efficiency tests for (a) d-PAHs and (b) d-MPs

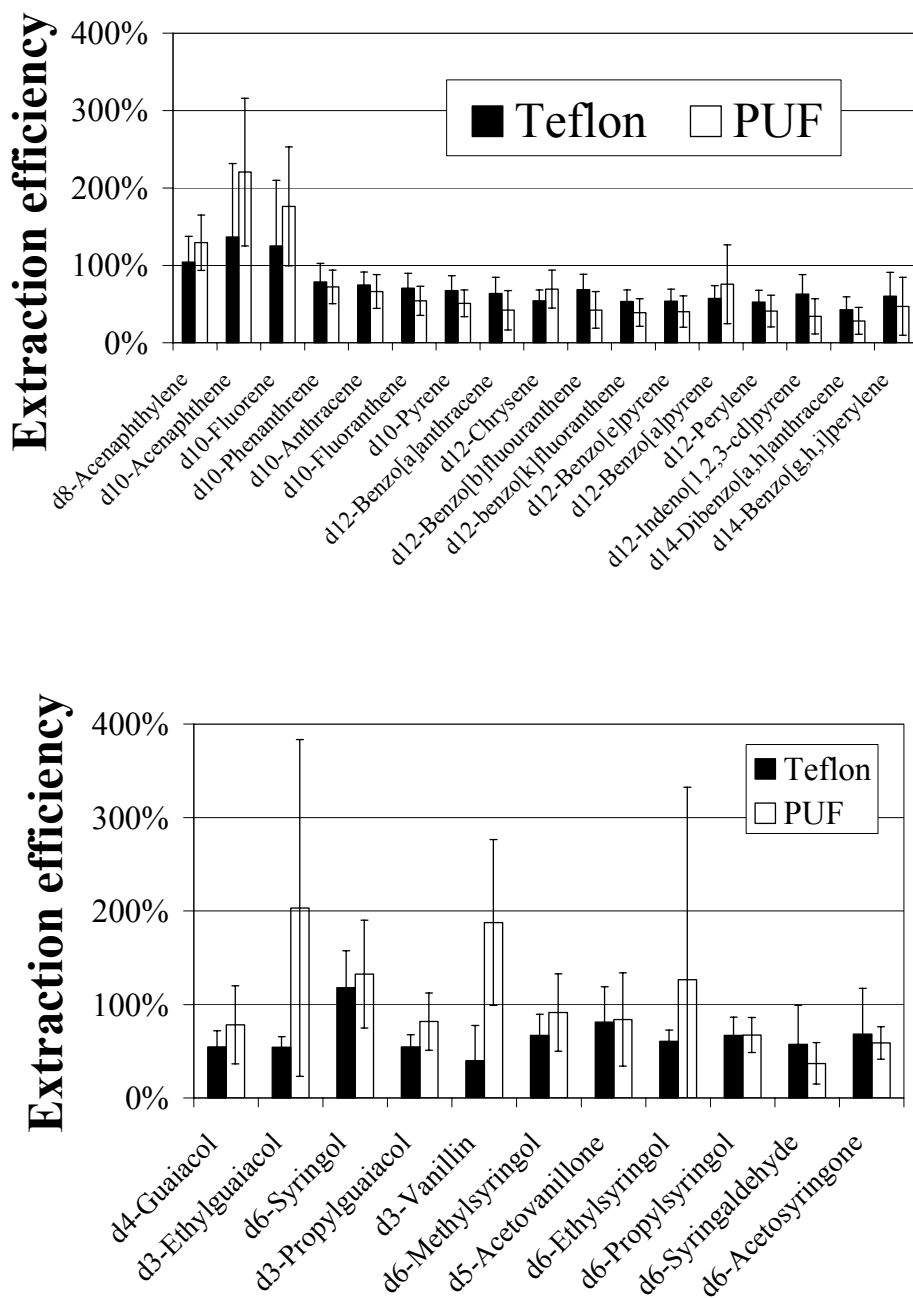Average PAH extraction efficiencies for UW samples were 74±32% (Teflon) and 74±39% (PUF). Extraction efficiencies for MPs were 66±27% (Teflon) and 104±69% (PUF). The high extraction efficiencies of the first 4 d-PAHs in Figure A.5a appear to be caused by an unidentified artifact in some samples and calibration standards, which also resulted in a proportional increase in the corresponding protonated analytes. Dividing by the sample- specific extraction efficiencies yielded reproducible concentrations. High PUF extraction efficiencies of d3-ethylguaiacol and d3-vanillin (Figure A.5b) are caused by 3 samples, the omission of which returns the extraction efficiencies to 100 (SD 22) and 132 (SD 60)% respectively.

Maddalena et al. (1998) report that the extraction efficiencies of 16 PAHs on PUF filters ranged between 83- 133% when extracted with a 4:1 cyclohexane: dichloromethane mixture. Keller and Bidleman (1984) report PAH extraction efficiencies of 103± 16% when PUFs were extracted with dichloromethane. McConnell and Bidleman (1998) report that the extraction efficiencies of chlorinated phenols and guaiacols trapped on PUFs ranged from 75- 101%, when extracted with 15% ethyl ether in petroleum ether. Hawthorne et al. (1992) performed multiple extractions of PUFs (with acetone) and quartz filters (with an acetone-dichloromethane mixture) spiked with deuterated alkanes, PAHs, phenols and MPs. The extraction efficiencies were reported to be > 90% for the first extract. Possible reasons for lower extraction efficiencies seen here include the use of a single extraction, and potential losses during sonication (temperatures reached 55ºC) and turbo- evaporation. However since data reported henceforth are corrected for sample- specific and species-specific extraction efficiencies, the losses during analysis are likely to be accounted for.

Deuterated standards were not available for 2 PAHs (retene and coronene) and the extraction efficiencies of the most structurally similar PAHs (d10-phenanthrene and d14-benzo[g,h,i]perylene respectively) were used to correct for losses during analysis instead. Since chrysene and triphenylene typically co-elute on standard 5,5-phenylmethylpolysiloxane capillary GC columns, their sum is reported here.

Deuterated analogues were unavailable for some MPs and the following substitutions were made: d5-acetovanilone for guaiacylacetone; d6-propylsyringol for allylsyringol; d3-vanillin for coniferylaldehyde; d6-acetosyringone for propyl and butylsyringone and d6-syringaldehyde for sinapylaldehyde. Since d-MPs were also unavailable for cis- and trans-isoeugenols and the linearity of their calibration curves was unsatisfactory, these two MPs are not discussed further. D3-methylguaiacol suffers from a co-elution artifact and d3-ethylguaiacol is used to calculate the extraction efficiency of methylguaiacol instead. Since PUFs with substantial loadings appear to contain a positive d3-eugenol artifact, d3-propylguaiacol is used to correct for eugenol losses during analysis.

A.3. SAMPLING PAHS ON QUARTZ FILTERS

To understand the extent of condensation on the quartz filters, PAHs on quartz and Teflon filters were compared with each other as shown in Figure A.6. Data relate to August 2001 samples only, and were analyzed at EWU.
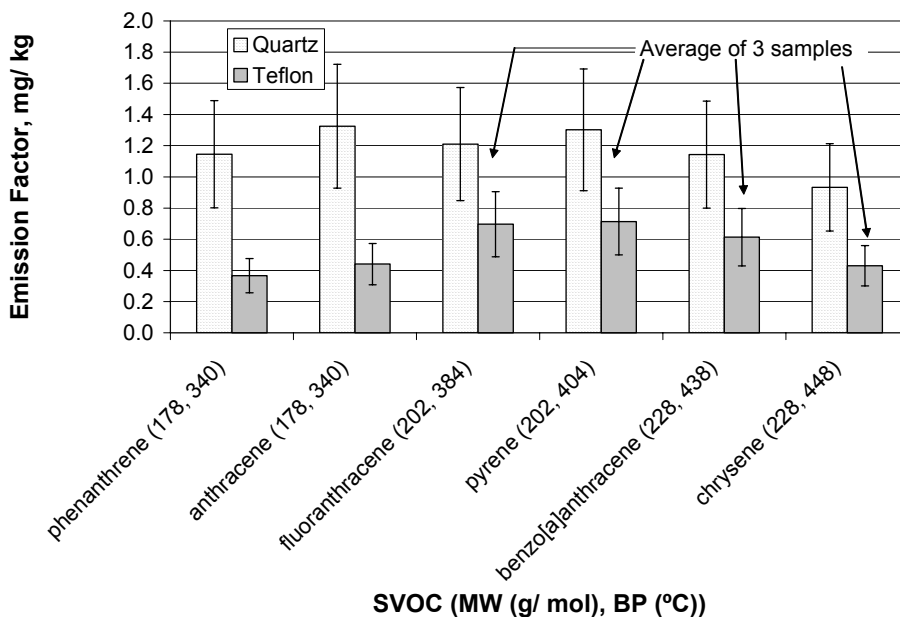
Figure A.6:   Comparison of PAHs seen on Teflon and Quartz filters from August 2001 wheat burns

The difference between PAHs on quartz and Teflon filters (= condensed phase PAH) was seen to reduce significantly as a function of PAH boiling point ($F_{1,5}$=11.8; P=0.026). This is expected since less volatile PAHs are likely to condense to a lesser extent.

A.4.   PHASE PARTITIONING OF SVOCS

It has been reported that a plot of Log[K_p] vs. 1/ absolute temperature [where K_p is the equilibrium partition coefficient, i.e. (solid phase SVOC concentration/ vapor phase SVOC concentration)/ particulate matter concentration] yielded a straight line for several individual SVOCs (Yamasaki et al., 1982; Keller and Bidleman, 1984; Jenkins et al., 1996). But none of the individual PAHs or MPs measured here followed this trend and the reasons are thought to be:

- Non-equilibrium at the time of sampling- the short time scales between emission and sampling in the chamber is probably insufficient for gas- vapor equilibrium. The formula

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is based on the assumption that gas- particle equilibrium is instantly attained and maintained (Calvert et al., 2002).

- Partitioning between solid and vapor phase may not be as predicted by theory, since the emission rate is changing throughout the burn cycle. The sum of all the instantaneous phase distributions may not necessarily add up to the solid-vapor concentrations averaged over the entire sampling period (Schauer et al., 1999).

- The above equation assumes adherence to the Langmuir isotherm (Yamasaki et al., 1982), and that the particle surface area available for SVOC adsorption affects the phase distribution (Venkataraman and Friedlander, 1994 and Hali et al, 1997). If SVOCs on particles exceeded monolayer coverage, or a variable fraction of surface sites were available for PAH adsorption, the assumptions therein would be invalid.

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APPENDIX B: LITERATURE SURVEY ON ISOKINETIC

SAMPLING OF PM$_{2.5}$

The purpose of isokinetic sampling is to draw air into the sampling train at the same rate it moves past the inlet. This ensures the moving sample air stream enters the sampling train with little or no disturbance to the streamlines. Once in the sampling tubes, the air must be slowed down to the desired rate whilst minimizing turbulence. Turbulence will cause particle losses to the tube walls. A substantial temperature change caused by friction with tube walls is likely to cause a loss of water from the particles (McMurry, 2000).

If the velocity of air into the sampling tube is lower than that of the aircraft, the divergence of streamlines at the inlet will result in the loss of smaller particles that have less momentum. If the air is being drawn at a linear velocity higher than the aircraft speed, the inability of the larger particles to follow the streamlines will result in the enrichment of smaller particles in the sample (McMurry, 2000). Sharp bends or long sampling hoses are not recommended. The entrance to the isokinetic sampling nozzle must be thin and tapered.

Application- specific linear velocities are required to achieve a particular cut point diameter (d$_{50}$). This places additional requirements on the air stream deceleration process. As a result researchers often sample TSP instead of PM$_{2.5}$ or PM$_{10}$ (ANE Pty. Ltd, 2003).

ANE Pty. Ltd., (2003) reported sampling TSP using Airmetrics Minivol samplers, fitted with near isokinetic inlets. These wind tunnel studies involved speeds up to 24 mph (lower than typical aircraft speeds). Fitz et al. (2004) reported using a DUSTrak PM monitor on top of a vehicle moving at speeds up to 60 mph. Isokinetic sampling was achieved with a computer controlled device that monitored the vehicle speed and vented the appropriate amount of excess air.

Bahreini et al. (2003) reported using a 100 μm critical orifice to draw air into an aerosol mass spectrometer (AMS) during the ACE- Asia campaigns. The main requirement here is a pump capable of maintaining a pressure drop in excess of 16 inches of mercury. Once the sample velocity reaches that of sound (the critical point), a further pressure drop does not cause a change in air flowrates. It is vital that the orifice does not become plugged with debris etc, for the correct airflow to be maintained. This may not be the most suitable method for sampling in plumes containing particles and ash.

Other isokinetic probes have been manufactured to suit specific applications (Annegarn et al., 1996- used on a Lear jet for speeds up to 550 km/ h). Szymanski et al. (1997) reported engineering a 3 stage virtual impactor into the isokinetic inlet. The point where the flow is divided was engineered so that particles larger than a certain size have too much momentum to follow the streamlines. Porous diffuser walls in conical inlets are often employed to allow excess air to diffuse away from the main sample stream, without causing much turbulence (McMurry, 2000; LTI website). Suction is applied across the diffuser, and this helps prevent the development of a turbulent boundary layer.

An isokinetic inlet to the DataRAM 2000 is available from Thermo Electron Corporation, for $750. This accessory is equipped with detachable inlet nozzles, designed for air streams moving as fast as 55 mph. A chart is available to help select the right nozzle and set the corresponding flowrate, so as to maintain the $PM_{2.5}$ cut point. The drawbacks are (i) aircrafts will find it hard to stay below 55mph during flight and (ii) the DR2000 has to be calibrated to gravimetric measurements made during each sample run.

Isokinetic probes for PM sampling should not be influenced by turbulence caused by the aircraft fuselage. Thus the inlet must be placed near the nose of the aircraft, which rules out the use of a single engine aircraft.

There appear to be no commercially available isokinetic inlets specifically designed for interfacing with the Airmetrics Minivol samplers. The adaptations of other designs require further research and testing in a wind tunnel.

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APPENDIX C: LITERATURE SURVEY ON DEGRADATION OF

PAH SAMPLES BY ATMOSPHERIC OXIDANTS

Ozone denuders were used in two field studies, the pertinent details of which are summarized below.

<u>Field study 1</u>

Source: Schauer et al. (2003)

Sampling location: urban and suburban Germany. RH ~ 75%, T= 10 ºC.

Sampling characteristics: 5 L/ min, 37 mm glass fiber filters, sampled for 1- 14 days.

Ambient O_3 concentration: 30- 50 ppb

Magnitude of negative artifact: Between 15- 35% for 5 and 6 ring PAHs, including benzo[a]pyrene (b[a]p). Data based on 9 samples, whose O_3 concentrations fall within 30- 50 ppb. The PAH loss increased linearly with the ambient O_3 concentration.

Other details: activated carbon denuder with an O_3 removal efficiency of ~ 90%, when sampling. The particle loss caused by the denuder was reported to be around 10%. The undenuded/ denuded ratios for 5 and 6 ring PAHs were found to depend on ambient O_3 levels. The duration of the sampling period was said to have negligible effect on the extent of PAH degradation, indicating that the PAH- O_3 reactions take place on time scales of minutes to hours (see section on "PAH degradation kinetics").

<u>Field Study 2</u>

Source: Tsapakis and Stephanou, (2003)

Sampling location: urban area in Crete. RH 64%, T= 26 ºC.

Sampling characteristics: 0.5 m^3/ min (linear velocity 75 cm s^{-1}), 20 x 25 cm glass fiber filter, sampling period 2 hours.

Ambient O$_3$ concentration: 56 ppb

Magnitude of negative artifact: See Table C.1.

Other details: Denuded and undenuded air was sampled at several sites and the O$_3$ degradation artifact was found to be a function of the O$_3$ concentration and sampling duration. The ratios of denuded/ undenuded samples are presented in Table C.1.

Table C.1:   Averaged ratios of denuded/ undenuded PAH samples collected at Heraklion (data based on 3 samples).

PAH	Particle phase den./ unden.	Vapor phase den./ unden.
Fluorene		**1.3**
Phenanthrene		**1.1**
Anthracene		**1.6**
Fluoranthene	**1.25**	**1.3**
Pyrene	1.81	**1.55**
Benzo[a]anthracene (b[a]a)	1.3	**1.35**
Chrysene	1.05	**1.15**
Benzo[b]fluoranthene (b[b]f)		**1.05**
Benzo[k]fluoranthene (b[k]f)	**1.05**	**1.1**
Benzo[a]pyrene (b[a]p)	2.24	

Note: Numbers in bold have been visually estimated from Figure 2 in paper.

Table C.1 shows that b[a]p and pyrene are the most reactive PAHs found in the solid phase, while pyrene and b[a]a are the most reactive PAHs found in the gas phase. Though not seen in the data collected at the Heraklion site, PAHs trapped on PUFs are degraded to a greater extent than PAHs trapped on glass fiber filters, probably due to the fact that PAH molecules on solid particles are somewhat shielded from contact with ambient air.

C.1. PAH DEGRADATION KINETICS

Pöschl et al. (2001) coated spark generated soot particles with benzo[a]pyrene and found that the O_3 induced degradation was much slower for multilayer surface coverage than for monolayer coverage. The explanation proposed, also echoed by Kamens et al. (1988) is that the PAHs on the outer surface are rapidly oxidized; the oxidation of the remaining PAH requires their diffusion to the surface from the sample bulk, or the diffusion of O_3 into the bulk. This is slower than the unhindered surface reaction and is therefore the rate limiting step. Kamens et al (1988) also reports faster degradation rates when collection media is loaded with low PAH concentrations (no multilayer coverage).

Therefore the initial decay rate in freshly emitted PAHs is likely to be faster than in aged aerosols, where the outermost layer has already been oxidized (Ulrich Pöschl, personal communication).

In the tests conducted by Pöschl et al. (2001), silica particles were coated with b[a]p (initial b[a]p concentration 600 ng m^{-3}) and exposed to 45 ppb O_3 in a chamber with residence times ranging from 30- 95 sec. Downstream of the chamber, a denuder was used to remove excess O_3 and the particles were deposited onto a glass fiber filter at a flowrate of 4.5 L min^{-1}. A 30% decline in b[a]p concentration was observed over 95 sec.

Table C.2 lists several rate constants and the corresponding half lives, as appearing in literature. Data are calculated from chamber experiments, and are corrected for chamber wall losses.

Table C.2: PAH- O_3 first order or pseudo first order reaction rate constants, when PAHs are exposed to 45 ppb O_3.

Source	Reaction rate constant, min^{-1}	Half life, min	Notes
Pöschl et al. (2001)	0.05	15.4	25% RH. B[a]p containing soot particles spread out on filter.
Wu et al. (1984)	0.06	11.8	B[a]p adsorbed on fused silica plates. Sample introduced directly into a fluorescence spectrometer.
Alebić- Juretić et al. (1990)	4.3×10^{-4} - 0.02	34- 1604	5 PAHs adsorbed on silica gel, with < monolayer coverage (low conc.). Rate constants valid for $[O_3]$ = 50- 200 ppb.

The following work, though not conducted at conditions comparable to ours, still reflects the negative PAH sampling artifact caused by O_3 induced oxidation:

- Van Vaeck and Cauwenberghe (1984) exposed diesel soot collected in duplicate on glass fiber filters to 1.5 ppm O_3 and observed declines ranging from 24- 77%, over 30 minutes. Half lives ranged from ~ 15 mins (b[a]p) to ~ 2 hrs (b[k]f).

- Peltonen and Kuljukka (1995) report that substantial PAH losses (in the order of a few percent to > 25%) were observed when filters were exposed to 140 ppb O_3.

- Tests conducted by passively exposing PAHs to 200 ppb O_3 in the dark (to mimic storage of filters) showed half lives ranging from 36 min- 53 hrs. (Finlayson- Pitts and Pitts, 2000).

C.2. EFFECTS OF HUMIDITY

Smoke particles are coated with liquid organic surfaces (Finlayson- Pitts and Pitts, 2000) and appear to behave differently to dry particles. Experiments involving dry silica particles (Alebić- Juretić et al., 1990), PAHs coated on filters (Finlayson- Pitts and Pitts,

2000) and spark discharged soot (Pöschl et al., 2001) show that high moisture levels reduce degradation of particle borne PAHs. It is thought that O_3 and H_2O molecules compete for the adsorption sites on the solid particles.

In contrast the Teflon chamber experiments conducted by Kamens et al. (1988) show that the PAHs on wood smoke particles degrade faster in environments of higher humidity. The mechanism is though to involve the formation of a thin aqueous film on the particle surface. O_3 would dissolve more easily in this layer and be transported to the PAH molecules. Since PAH solubility in water declines with increasing molecular mass (Seinfeld and Pandis, 1997), the lower molecular weight PAHs are likely to be degraded more by O_3, in the presence of higher humidity.

C.3. O_3 DENUDER

- The use of an activated carbon denuder by Schauer et al. (2003) is not very appropriate since it is capable of removing some of the gas phase PAHs too. However that study concentrated on heavier PAHs that predominantly reside in the particle phase and therefore the results are not likely to be influenced.

- Tsapakis and Stephanou (2003) reported using a water/ glycerol- KNO_2 denuder that was shown to have 90% O_3 removal efficiency at the sampling flowrate of 0.5 m^3/ min. At flows characteristic of lo- vol samplers, it is reported to have > 98% O_3 removal efficiency.

- Saturated KI solutions have been used widely as O_3 absorbers, as KI traps all atmospheric oxidants (Koutrakis et al., 1993).

C.4.   REFERENCES

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