AEROSOL CHARACTERIZATION FOR AGRICULTURAL FIELD BURNING SMOKE

By

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To the Faculty of Washington State University:

The members of the Committee appointed to examine the dissertation of JORGE RODRIGO JIMENEZ find it satisfactory and recommend that it be accepted.

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AEROSOL CHARACTERIZATION FOR AGRICULTURAL FIELD BURNING SMOKE

Abstract

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Rural communities in eastern Washington and northern Idaho have been concerned about health problems related to smoke exposure from agricultural field burning. However, pollution from field burning often does not violate air quality standards, and not much is known about community exposure to smoke from field burning. This research improves the understanding of air quality impacts from regional agricultural field burning in these communities.

$PM_{2.5}$ measurements were made at a monitoring site established in Pullman, WA during the fall 2002. Two source-receptor models were used to apportion $PM_{2.5}$ from vegetative burning smoke. Contributions of $PM_{2.5}$ from soil (38%), vegetative burning (35%), and sulfate aerosol (20%), and much less from vehicles (2%) and cooking (1%) were found in the Pullman airshed.

However, the source profile for vegetative burning used in the previous study was not able to differentiate agricultural residue smoke versus smoke from woodstoves. Levoglucosan and 19 methoxyphenols (MPs) were evaluated as tracers for wheat and

Kentucky bluegrass (KBG) stubble smoke. PM samples from wheat and KBG stubble smoke were collected from controlled chamber burns, and field burns in the region. Among the MPs analyzed in this work, syringaldehyde, acetosyringone and coniferylaldehyde were found to be the most prominent tracers for wheat smoke, and were not always present in detectable amounts in KBG smoke, while the ratio of LG/ syringaldehyde found in wheat stubble (~80) was much higher than the same ratio reported for hardwood (~5).

During the Pullman study, the continuous $PM_{2.5}$ measurements alone were not able to distinguish vegetative combustion from soil originated PM. In addition to $PM_{2.5}$ monitors, an aethalometer was used to make this distinction. This instrument is a semi-continuous monitor that indirectly measures light absorbing carbon (LAC) aerosol concentrations by measuring light absorption through a quartz filter.

Evidence indicates that the aethalometer may be affected by semi-volatile organic compounds (SVOC), multiple scattering, and a non-linear response to highly absorbing particles. In order to quantify and correct for these interferences, the aethalometer was tested with a SVOC denuder at controlled conditions of PM from Diesel exhaust and a correction was proposed for measuring near-real time concentrations of BC from freshly emitted soot.

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ATTRIBUTION

This dissertation includes five chapters. The first chapter presents the objectives and motivation for the research included in the three following chapters. Chapters 2, 3 and 4 consist of individual self-standing manuscripts outlining and addressing specific aspects of the overall research pursued in this dissertation. These chapters are formatted to meet the requirements of peer reviewed scientific journals relevant to the field. The last chapter, Chapter 5, summarizes the finding of this work and outlines the conclusions and recommendations for the overall goals of this research.

I am the primary author of each of the chapters presented in this dissertation. In addition, I had primary responsibility for the analyses and results presented in the formatted manuscript chapters. Others made important contributions as indicated below.

CHAPTER 2: Agricultural Burning Smoke in Eastern Washington: Part I. Atmospheric Characterization

This chapter was part of a larger study designed from the cooperative effort between The Northwest Center for Particulate Air Pollution and Health, University of Washington and Washington State University through L.-J. Sally Liu, Candis Claiborn, J. Kaufman, J. Koenig, Jeff Sullivan, and Carol Trenga. Additional support and assistance in study design was provided by Grant Pfeifer and Karen Wood of the Washington Department of Ecology.

Operation, data collection, and calibration of instrumentation of a central monitoring site in Pullman, WA were carried out by Jorge Jiménez, Tim Gould, Mark Hoffman, Dennis Finn and Lee Bamesberger. Additional help and support was provided by

Ranil Dhammapala, Kristie Schumaker, and Sara Jarvis during the data collection stage. Jorge Jiménez conducted the source apportionment modeling using data collected at the monitoring site. Candis Claiborn, Sally Liu, and Tim Larson provided expertise in developing the models and interpreting the results from the source receptor model.

CHAPTER 3: Developing a Source Fingerprint for Burning of Wheat and Kentucky bluegrass Stubble in Eastern Washington and Northern Idaho

Jorge Jiménez and Ranil Dhammapala collected and analyzed the smoke samples from wheat and Kentucky bluegrass stubble burning. Karen Hirakawa helped in collecting samples from controlled chamber experiments at the EPA facilities in North Carolina. Shawn Nolph from the Washington State Department of Ecology and Julie Simpson from the Nez Perce tribe helped in coordinating the prescribed burns for our fieldwork. Mike Paulsen and Melissa Zgola helped in the preparation of the collected samples for analysis of organic tracers. Candis Claiborn and Christopher Simpson provided expertise in interpreting the results of the analysis. Similarly, Brian Lamb and Hal Westberg provided meaningful comments and suggestions for the analysis during the preliminary examination.

CHAPTER 4: Developing a Correction for Measuring Real-time Behavior of Fresh Diesel Soot Concentrations by Means of Aethalometer

Jorge Jiménez designed the experiments, collected data and developed the model to correct the aethalometer algorithm in order to measure near real-time concentrations

of strong light absorbing aerosols, such as Diesel soot. Tim Gould, Jim Stewart, and Ammena Gill provided additional help and support to operate the instruments and collect data at the EPA Northwest Center for Particulate Air Pollution and Health Diesel Chamber. Lara Gundel provided help and expertise to run experiments at Lawrence Berkeley National Laboratory in Berkeley, CA. Candis Claiborn, Tim Larson, and Tom Kirchstetter provided expertise in developing the correction for the aethalometer from the Diesel chamber experiment.

CHAPTER 1: INTRODUCTION

For many years, cereal grain and grass seed farmers in eastern Washington and northern Idaho have been utilizing prescribed field burning as part of their farming practices. They grow commercial species such as wheat, barley and grass seed and the choice of burning to clear fields of vegetation and debris has long been an inexpensive and efficient way to prepare the ground for farming activities. The main purposes of burning are to: (a) eliminate surface organic matter; (b) control undesirable weeds; (c) control plant pests and diseases; (d) return nutrients and minerals to the soil; and (e) promote seed production of the crop (Meland and Boubel, 1966). However, neighboring communities in rural areas have noticed an impact in the air quality from these burning practices (Jimenez, 2002). In addition, people have reported health related problems, which include asthma, headaches, and other respiratory and heart conditions (Roberts and Corkill, 1998).

In 1998, the Washington Department of Ecology (WDOE) prohibited the utilization of fire as a tool to clear grass seed fields in the state of Washington. However, grass seed production (Kentucky bluegrass, KBG) using fire is still allowed in Idaho and Oregon, where grass field burning regulations differ from those in Washington State (WDOE, 1998). After WDOE banned KBG burning in Washington, citizen complaints have been directed at other burning activities such as wheat and barley stubble. Currently, field burning is regulated in Washington State and allowed when ventilation conditions disperse the smoke away from urban areas. Yet, rural communities have complained of impacts on air quality from current burning practices, and citizens have voiced health

concerns related to smoke exposure, as well as potentially negative impacts on tourism and economic activities.

Biomass smoke includes both vapor and particulate phase material, with much of the particulate matter (PM) in the $PM_{2.5}$ (PM less than 2.5 μm in aerodynamic diameter) size range. $PM_{2.5}$ from biomass smoke consists mainly of organic carbonaceous species (OC) and elemental carbon (EC). Elemental carbon is also referred to as light absorbing carbon (LAC) or black carbon (BC) aerosol from its optical property as a strong light absorber. These compounds are by-products from incomplete combustion of carbonaceous fuels. In addition to smoke from agricultural field burning, eastern Washington, a semi-arid region, can have significant levels of particles in the air from a variety of sources. These sources include fugitive dust from roads and fields (Claiborn et al., 2000; Kim et al., 2003), and forest fires (Jimenez, 2002).

$PM_{2.5}$ in biomass burning smoke can have a potentially detrimental impact on human health from both acute and chronic exposures (US EPA, 2004). Chronic exposure to biomass smoke could reduce lung function, depress the immune system and increase the risk of respiratory diseases (Sutherland, 2004; Sutherland and Martin, 2003). In addition, there is evidence that short-term excursions in $PM_{2.5}$ result in acute health effects on susceptible people; including chronic obstructive pulmonary disease (COPD) patients, and asthmatic children (Romieu et al., 1996; Pekkanen et al., 1997; Peters et al., 1997). Long and co-workers (1998) reported from their questionnaire-based survey in Winnipeg, Canada that individuals with asthma or chronic bronchitis were adversely affected by straw burning. More recently, Tirigoe et al. (2000) found a relationship

between PM_{10} (PM less than 10 μm in aerodynamic diameter) and children with asthma attacks, with the rise of PM_{10} most likely from rice straw burning in Niigata, Japan.

Since the National Ambient Air Quality Standards (NAAQS) for PM_{10} and $PM_{2.5}$ are based on 24-h or annual average concentrations, these smoke episodes do not necessarily violate the standards due to their relatively short duration and the scarcity of the monitors in eastern Washington and northern Idaho. Thus, few studies have been conducted to characterize air quality during agricultural burning episodes and even fewer have characterized exposure and the associated health effects. As populations in the rural areas of eastern Washington and northern Idaho continue to grow, there is a need for an improved understanding of the air quality impacts of agricultural field burning on populated areas. Our efforts to characterize the community exposure to smoke from agricultural field burning motivated the research presented in Chapter 2, which is the first paper of a series of three publications (Jimenez et al., 2006; Wu et al., 2006; Sullivan et al., 2006) generated from a study examining community exposure to air pollution from agricultural burning and the related health effects in a susceptible group, which involved a selected group of adults with mild to moderate asthma.

Chapter 2 characterizes the air quality during a period of prescribed agricultural field burning in an eastern Washington town. As part of this research, two source-receptor models were used to estimate smoke intrusion from regional agricultural field burning on the observed $PM_{2.5}$ mass concentrations in Pullman, WA. Apportioning smoke from agricultural field burning in populated areas through the use of receptor models can be accomplished by knowing the chemical and physical characteristics of the particle tracers present in smoke. Other sources of biomass smoke, including residential wood

stoves and forest fires, affect the ability of these models to accurately apportion this source due to common tracers and the similarity of the emission profiles (Simoneit, 2002; Oros and Simoneit, 2001). Thus, we were interested in identifying unique and reliable tracers for wheat and/or grass smoke to successfully separate and apportion air pollution from combustion of crop residues. This was the motivation for the research presented in Chapter 3, which has been submitted for publication in the Journal *Environmental Science & Technology*.

An important aspect of measuring short-term excursions in $PM_{2.5}$ from field burning is capturing real-time characteristic of biomass smoke in the air. Filter-based samples collected over time do not often capture short-term variations and current continuous PM monitors; such as Tapered Element Oscillating Microbalance (TEOM) and light scattering nephelometer do not provide much information regarding the origin of the particles sampled (fine airborne dust versus biomass smoke). Since we know that biomass burning is a source of carbonaceous aerosols, real-time concentrations of BC can be measured using an aethalometer (Magee Scientific, Berkeley, CA), which is a near-continuous instrument that measures BC aerosol concentrations from its light absorption properties through a quartz filter at one or more different wavelengths (Hansen et al., 1984). Nonetheless, evidence indicates that quartz fiber filters are prone to absorb semi-volatile organic compounds (SVOC) (Eatough et al., 1995; Pang et al., 2002), which are also known to absorb light at several wavelengths (Weingartner et al., 2003). This condition may result in over-estimations of BC in environments with high SVOC concentrations. This instrumental artifact was the motivation for the research presented in Chapter 4 and the manuscript was formatted in the style of the *Journal of the Air &*

Waste Management Association. In addition, this Chapter proposes a correction for the current aethalometer algorithm, in order to measure BC from fresh Diesel exhaust.

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Chapter 2

Agricultural Burning Smoke in Eastern Washington: Part I. Atmospheric Characterization

Agricultural Burning Smoke in Eastern Washington: Part I. Atmospheric Characterization

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ABSTRACT

Agricultural burning has been subject to intense debate in eastern Washington. Rural communities are concerned about health impacts related to smoke exposure from field burning. However, the short-duration excursions of smoke often do not violate air quality standards at locations where air quality monitors are situated. The purpose of this study was to characterize the air quality in Pullman, WA during the fall 2002 prescribed field burning season, as part of a larger study conducted to examine community exposure to agricultural burning smoke and the related short-term health effects. Data collected included continuous $PM_{2.5}$, PM_{10}, CO_2, nitrogen oxides, and 12-hour integrated $PM_{2.5}$, OC, EC, and levoglucosan (a biomass burning marker). Four episodes were defined when three consecutive 30-min $PM_{2.5}$ averages exceeded 40 μg m^{-3}. Two source-receptor models; the Chemical Mass Balance model (CMB) and Positive Matrix Factorization (PMF) were used to estimate smoke intrusion from regional agricultural burning. During this study, the average $PM_{2.5}$, OC, and EC were similar during the daytime and nighttime, while LG was twice as high during the night. The CMB results showed major contributions of $PM_{2.5}$ from soil (38%), vegetative burning (35%), and sulfate aerosol (20%), and much less from vehicles (2%), and cooking (1%). The 3-source profiles generated by PMF were consistent with those selected for CMB modeling. The $PM_{2.5}$ estimates from these two models were highly correlated for individual sources. The LG, NOx, CO_2, OC, and apportioned $PM_{2.5}$ from vegetative burning and soil were higher during the episodes than during non-episode days, while EC and $PM_{2.5}$ from secondary sulfate, vehicles, and cooking sources were similar throughout the study. We

characterized the episodes of agricultural field burning with elevated LG, OC, and biomass burning contributions to $PM_{2.5}$.

Keywords: Biomass burning, smoke impact in rural communities, source apportionment, exposure assessment, receptor model.

2.1 INTRODUCTION

In the past decade, agricultural burning has been subject to intense discussion and public debate in the semi-arid eastern Washington (Jimenez, 2002). Neighboring communities from rural areas have noticed an impact on air quality from farmers' burning practices and citizens have voiced health concerns related to smoke exposure, as well as potentially negative impacts on tourism and economic activities (Roberts and Corkill, 1998). Smoke from biomass burning contains numerous chemical compounds including, but not limited to, carbon monoxide (CO), NO_x, volatile organic compounds (Jenkins et al., 1996), and particulate matter with an aerodynamic diameter less than 2.5 μm ($PM_{2.5}$). In eastern Washington, other than agricultural field burning, there are several important sources of $PM_{2.5}$ including regional forest fires and fugitive dust from roads and occasional wind blown dust (Claiborn et al., 2000; Kim et al., 2003). Fugitive dust in this region contains a significant portion of geological material, and overlaps the $PM_{2.5}$ at aerodynamic diameters between 1 and 3 μm (Claiborn et al., 2000).

$PM_{2.5}$ in biomass burning smoke can have a potentially detrimental impact on human health from both acute and chronic exposures (US EPA, 2004). Chronic exposure to biomass smoke could reduce lung function, depress the immune system and increase

the risk of respiratory diseases (Sutherland, 2004; Sutherland and Martin, 2003). There is evidence that short-term excursions in $PM_{2.5}$ result in acute health effects on susceptible people including COPD, cardiovascular patients, and asthmatic children (Romieu et al., 1996; Pekkanen et al., 1997; Peters et al., 1997; Vedal et al., 1998; Roemer et al., 2000; Yu et al., 2000; Ostro et al., 2001; Delfino et al., 2002; Delfino et al., 2003). The health effects include coughing, wheezing, chest tightness, and shortness of breath. Long and coworker (1998) reported from their questionnaire-based survey in Winnipeg, Canada that individuals with asthma or chronic bronchitis were more likely to be affected by straw burning. Tirigoe et al. (2000) also found a relationship between PM_{10} and children with asthma attacks, with the rise of PM_{10} most likely from rice straw burning in Niigata, Japan. However, short-term $PM_{2.5}$ excursions are not currently regulated.

Agricultural burning in eastern Washington occurs primarily in the spring and fall, involving burning of mainly residues of cereal grain including wheat and barley. Approximately 2,000 agricultural fires are set each year in Washington State (WA DOE, 2004) over an area of ~ 15,000 Km^2, with a total population of ~160,000 (WDOE, 2004). However, only 6 monitoring sites report real-time $PM_{2.5}$ concentrations in this area. This small number of monitoring sites likely result in an inadequate monitoring of smoke episodes under varying meteorological conditions. Evidence was provided by the disagreement between the $PM_{2.5}$ measurements and the amount of land burned or the number of smoke related complaints (Jimenez, 2002). Since the NAAQS for PM_{10} and $PM_{2.5}$ are based on 24-h or annual average concentrations, these smoke episodes do not necessarily violate the NAAQS due to their relatively short duration and the scarcity of the monitors in eastern Washington. Thus, few studies have been conducted to

characterize air quality during agricultural burning episodes and even less about the associated health effects.

The purpose of this study was to characterize air quality during a period of prescribed agricultural field burning in an eastern Washington town, as part of a larger study examining community exposure to agricultural burning smoke and the related health effects. As part of this work, two source-receptor models were used to estimate the impacts of smoke intrusion from regional agricultural field burning on the observed $PM_{2.5}$ mass concentrations in Pullman.

2.2 METHODS

2.2.1. Monitoring period and site selection

This study was conducted in the 2002 fall agricultural burning season (September–November) based on the historical evidence for greater amounts of acres burned per day and more smoke episodes reported by citizens in the fall burning season (Jimenez, 2002). The air quality measurements analyzed in this paper were collected primarily at one central monitoring site located on the roof of a building at Washington State University (WSU) in Pullman, WA (elevation= 770 m, approximately 12 m above street level). Measurements from this site were used to represent the ambient exposure of subjects on the WSU campus (average elevation= 768 m) and in the general Pullman area (average elevation= 774 m). In addition, we used this data, along with measurements collected inside the study subjects' residences and time-location-activity information to estimate personal exposures to $PM_{2.5}$ from outdoor sources and from agriculture burning smoke using a random component superposition model, a recursive mass balance model,

and a total exposure model. This analysis is reported elsewhere (Wu et al., 2005). The distance from the monitoring site to the burning fields depended on the location of the field relative to the monitoring site, which ranged from a few to 200 kilometers.

2.2.2. Air quality sampling

PM measurements were taken from a continuous PM_{10} and $PM_{2.5}$ Tapered Element Oscillating Microbalance (TEOM) monitors (30-min averages. Series 1400a, Thermo Electron Co), a light scattering nephelometer (10-min averages. M903, Radiance Research, Seattle, WA), and a DataRAM with a $PM_{2.5}$ size-selective inlet (10-min averages, Thermo-Andersen, Smyrna, GA). In addition, 12-h integrated $PM_{2.5}$ samples (operated from 0800 to 2000 and from 2000 to 0800, PST) were taken from collocated and triplicate single-stage 10-LPM Harvard Impactors ($HI_{2.5}$) (Air Diagnostics Inc., Naples, ME). Two $HI_{2.5}$ sampled $PM_{2.5}$ onto 37-mm Teflon filters, and the third sampled onto a quartz filter. The nephelometer was calibrated against the $HI_{2.5}$ measurements (intercept= 0.134 $x10^{-5}$ m^{-1}, slope= 0.243 x 10^{-5} m^2 μg^{-1}, R^2 = 0.83, N= 99). Other air constituents included continuous carbon dioxide (10-min average, Telaire 1050 Engelhard, Goleta, CA), nitrogen oxides (10-min average, model 42 Thermal Environmental Instruments, Inc), and carbon monoxide (10-min average, Model 9830 Monitor Labs, Inc). Meteorological parameters including temperature, humidity, wind speed and wind direction were also recorded using a small weather station (30-min average, WeatherLink, Davis Instruments Corp. Hayward, CA 94545).

The PM collected on the Teflon media was analyzed gravimetrically using a Mettler-Toledo UMT2 microbalance at the University of Washington laboratory, at a

constant temperature (22.2 ±1.8°C) and relative humidity (34.8 ±2.5%) for at least 24 hours prior to weighing (Allen et al., 2001). Filters were then analyzed for 55 inorganic elements using X-ray Fluorescence (XRF) at Chester LabNet, Tigard, Oregon. One set of the duplicate Teflon filters were extracted by ultrasonication in ethylacetate/triethylamine for LG analysis using Gas Chromatography – Mass Spectrometry (GC-MS) (Simpson et al., 2004). Sections of the quartz filters (1 cm^2) were analyzed for OC and EC via Thermal Optical Transmittance (Sunset Laboratory, Inc. Tigard, OR) using a modified version of the NIOSH 5040 method (Pang et al., 2002).

2.2.3. Episode definition

An episode was declared when three or more 30-minute average $PM_{2.5}$ concentrations exceeded 40 µg m^{-3} during any 24-hour period according to the central site $PM_{2.5}$ TEOM and/or DataRAM measurements. This threshold value was selected based on the frequency of historical (2000 and 2001) hourly nephelometer $PM_{2.5}$ readings exceeding this magnitude at the downtown Pullman air quality monitoring site operated by the Washington State Department of Ecology (WDOE) (see Table 1). Our previous study (Jimenez, 2002) also found a link between these exceedances and vegetative burning smoke episodes in Pullman. Episode declamation was aided by visual observations of agricultural burning smoke plumes that were not upwind of the central site monitors; current and predicted meteorological conditions that may favor the occurrence of an episode; and the WDOE's daily morning burn calls for neighboring regions. This study also included a single-sided blind sham episode (not a smoke episode) declared during a period of relatively low $PM_{2.5}$ in order to compare the subject

health effect responses with true episode periods. A declared episode triggered three consecutive days of intensive health effect monitoring (for more details on the exposure and health assessments, see Wu et al., 2005; Sullivan et al., 2005).

2.2.4. Quality control

Field blanks and duplicates were deployed so that they comprised at least 10% of the total $HI_{2.5}$ sample size. The precision (1.2 μg m^{-3}) and accuracy (3%) of the $HI_{2.5}$ have been reported in a previous paper (Liu et al. 2003). Filters were analyzed for LG in batches of approximately 20 filters. In each batch, two laboratory blanks and 4 spiked samples (with d^7-levoglucosan in the extracts) were analyzed. The overall recovery based on the spiked samples was 75 11%. The analytical precision based on 10-15% of samples analyzed in duplicate was 24%. Among the 104 samples analyzed for LG, 9 samples were below the limit of detection (LOD ~ 1.4 ng m^{-3}) and two samples had fatal analytical errors (unacceptably low recoveries, failure to derivatize, or chromatographic interferences).

2.2.5. Data analysis

The collected data for PM, gaseous pollutants, and particulate carbonaceous species at the central site were tested for normality and non-normally distributed data were conformed using the Box-Cox conformation (Box and Cox, 1964). Statistical differences between episode and non-episode periods in pollution levels were tested using a one-tailed two-sample t-test. Source apportioned $PM_{2.5}$ mass concentrations (described below) were also compared between the episode and non-episode periods.

Data used for source apportionment analysis were subjected to several constraints and consistency checks. $HI_{2.5}$ measurements were compared to those from the $TEOM_{2.5}$ and to the reconstructed fine mass (RCFM), which is defined as the sum of the individual components of fine PM fractions from each chemical analysis; i.e. OC, EC and inorganic elements (Malm et al., 1994)

$$RCFM = 1.6 \times [OC] + [EC] + [sulfate] + [nitrate] + [soil] + [others] \quad .....(1)$$

where the brackets denote mass concentrations (μg m^{-3}) of each component. "Soil" corresponds to the sum of elements predominately associated with soil (Fe, Al, Si, Ca, and Ti), plus oxygen for the oxidized state of these elements (AL_2O_3, SiO, CaO, FeO, Fe_2O_3, TiO_2).

$$Soil = 2.20 \times [Al] + 2.49[Si] + 1.63[Ca] + 2.42[Fe] + 1.94[Ti] \quad .....(2)$$

"Others" represents all other elements that were analyzed. RCFM was calculated for all 12-hour samples based on the XRF and EC/OC results and compared to the observed $HI_{2.5}$ mass concentration.

For source apportionment, we used the US EPA's Chemical Mass Balance receptor model Version 8 (CMB) (Watson et al., 2001). The inputs to the CMB model were the $PM_{2.5}$ chemical composition data, the mass fraction of the chemical species in the source profiles, and the uncertainties of individual species. Chemical species with large uncertainties have less influence in the solution because in the fitting procedure they are not weighed as much as those more precisely measured species or unique tracers. The sources of $PM_{2.5}$ selected in the CMB model included airborne dust (soil), vegetative

burning smoke, secondary sulfate aerosol, vehicular traffic, and cooking fumes. The soil and sulfate aerosol profiles were derived from the Spokane dust profile (Core et al., 1982) and a previous source apportionment study in Spokane (Kim et al., 2003). The vegetative burning smoke profile was derived from a previous source apportionment study in Spokane (Hoffman, 2002) and other documented studies of emission factors for wood smoke reporting LG (Oros and Simoneit, 2001; Oros and Simoneit, 2001b). We also included profiles documented in the receptor model source composition library (U.S. EPA-450/4-85-002) for vehicular traffic (Cass and McRae, 1981) and cooking fumes (Hildemann et al., 1991). The chemical tracers considered for modeling were Al, Br, Ca, Cl, Cu, OC, EC, Fe, K, Mg, S, Si, SO4, Ti, Zn and LG. We excluded other elements with more than 70% samples below detection limit.

In addition to the CMB model, we also applied the positive matrix factorization model (PMF) for source apportionment. The PMF model is a statistical model that adopts a weighted least-squares approach to solve the factor analysis problem and does not require prior knowledge of the source profiles (Paatero, 1997). We followed the procedure of Polissar et al. (2001) and Maykut et al. (2003) to generate the PMF model inputs and assign uncertainties to each measurement. We examined both a three-source (3S) and a four-source (4S) model, and tested various FPEAK parameters, ranging from -0.8 to 0.8 with increments of 0.1 (Paatero, 1997; Maykut et al., 2003). The 'Q values' indicated that FPEAK values between -0.4 and 0.1 provided the optimum solutions for both models. After the source contribution factors were determined by PMF, they were re-scaled by regressing them against the corresponding $PM_{2.5}$ mass concentrations to obtain both the source-specific $PM_{2.5}$ mass contributions and mass fraction based source

profiles. The 4-source PMF model identified one more source, "others," in addition to the three identified by the 3-source PMF model. However, the use of PMF in this study is limited by the small sample size (N=123). When we forced the PMF to produce 4 sources, we artificially introduced errors. The 3-source PMF model provided results that were more consistent with the CMB results than the 4-source PMF model, so the 4-source model was not analyzed further

2.3 RESULTS & DISCUSSION

2.3.1. Air quality measurements

The $TEOM_{2.5}$, $TEOM_{10}$, and nephelometer data (September - October 2002) are shown in Figure 1. During several episodes, $TEOM_{2.5}$ measurements spiked above 40 $\mu g/m^3$ and triggered two episode calls, including the periods of Sept 11-15 during which two consecutive episode calls were made, and Oct 17-19. Two episodes that were not declared occurred during Sept 25-26 and Oct 24-26. A sham episode was declared for Oct 9-11. The $TEOM_{2.5}$ was not functioning from 9/28 to 10/17, during which period the nephelometer data was used instead. Table 2 summarizes the measurements of PM and gaseous pollutants (CO_2, CO and NO_x). The mean PM_{10} and $PM_{2.5}$ levels were 40.5 ±38.8, 13.6 ±9.4 (TEOM), and 11.3 ±7.9 $\mu g\ m^{-3}$ (nephelometer), respectively, with $TEOM_{2.5}$ exceeding 40 $\mu g\ m^{-3}$ for 38 30-min periods, while the nephelometer recorded 9 30-min periods exceeding 40 $\mu g\ m^{-3}$. The discrepancy in peak values between $TEOM_{2.5}$ and nephelometer is discussed later. Note that there were only 4 exceedances recorded by the nephelometer located near downtown Pullman (Table 1). The difference in the number of exceedances between the downtown and WSU sites could be due partially to

the spatial variation. The DOE site was located in a residential area (~ 1 km away from the WSU site) with less vehicular traffic and facing a different direction relative to our central site. The DOE site was also slightly higher than the WSU site, which may result in lower concentrations (Wu et al., 2005).

Table 3 summarizes the 12-h integrated $PM_{2.5}$, OC, EC, LG, and trace element concentrations. The mean nighttime values were higher than the daytime values for $PM_{2.5}$ ($p<0.01$), LG ($p<0.01$) and for Si, Al, S, Ca, K and Mg ($p<0.01$). These differences could be due to the effect of nighttime inversions with limited vertical mixing and/or nighttime residential wood burning. However, based on the 2000 census data, there were only 30 (0.3%) homes in Pullman using wood as a heating source. The regression analysis between RCFM and $HI_{2.5}$ (intercept= 0.31, slope= 0.93, R^2= 0.89, N= 123) showed a good consistency between the reconstructed $PM_{2.5}$ and the actual gravimetric $PM_{2.5}$ mass concentrations. Our LG measurements (mean= 74 ng m^{-3}, range 2-327 ng m^{-3}) were comparable to measurements obtained in Israel, mean ~73 ng m^{-3} (Graham et al., 2004) and higher than those observed in Brazil during rice and sugar cane crop burning, 1.65-7.45 ng/m^3 (Santos et al., 2004) and 0.15-28.42 ng m^{-3} (Santos et al., 2002), and Nigeria, 0.04-3.3 ng/m^3 (Stanley and Simoneit, 1990; Simoneit et al., 1988). However, our observations were lower than those detected in U.S. urban areas, 280-4860 ng m^{-3} and 200-1200 ng m^{-3} (Simoneit et al., 1993; Simoneit et al., 1999; Nolte et al., 2002; Fraser and Lakshmanan, 2000), and far below those observed during severe episodes of biomass smoke pollution from agricultural slash and burning in Southeast Asia, 1400-40240 ng m^{-3} (Radzi Bin Bas et al., 2004). To date, there have not been specifically reported LG

levels from wheat stubble burning. Thus the differences between our observed LG levels and others could also be due to the type of wood/crops burned.

The correlations between air pollutants are summarized in Table 4. The Pearson's correlation coefficients, which were consistent with the Spearman's coefficients were high for the $TEOM_{10}$ and $TEOM_{2.5}$ ($r= 0.84$), $TEOM_{2.5}$ and $HI_{2.5}$ ($r= 0.82$), and Neph and $HI_{2.5}$ ($r=0.81$). The lower Pearson's correlation between the 30-minute average Neph and $TEOM_{2.5}$ ($r= 0.71$) was due to the observed low concentrations, shorter averaging time, and the fact that the aerosol characteristics and the particle scattering efficiency could differ during these episodes (Liu et al., 2002). The differences found between the $TEOM_{2.5}$ and $HI_{2.5}$ mass concentration could be due to the higher uncertainties at low $PM_{2.5}$ concentrations and a possible overestimation on $TEOM_{2.5}$ equipped with a URG cyclone (Moore and McFarland, 1993). During a performance study under different loading conditions, it was reported that the URG type cyclone had a very shallow particle size selection curve and was likely to overestimate $PM_{2.5}$ concentrations when sampling coarse aerosols (Kenny, 1998). With a significant contribution of dust aerosols in our study area, this inlet artifact may partially account for the difference found between the $TEOM_{2.5}$ and the $HI_{2.5}$.

NOx, OC, and LG were also correlated with $HI_{2.5}$ ($r>0.47$, $p< 0.01$), suggesting that some of the $PM_{2.5}$ was related to vegetative combustion sources. Concentrations of EC and CO_2 during episodes were not different from those during non-episode periods and also showed the least correlations with other parameters. We did not find a strong correlation ($r =0.27$, $p<0.05$) between humidity and PM, nor for wind speed and apportioned airborne dust ($r =-0.37$, $p<0.05$). We had expected contribution of airborne

dust from adjacent fields and from roads (vehicular traffic) at low relative humidity and high wind speed under the right wind direction. This negative correlation between wind speed and airborne dust showed that not necessarily all observed dust was suspended in the air due to the effect of wind.

2.3.2. Source apportionment

CMB model

Figure 2 shows the chemical profiles for the five sources used in the CMB model. LG was used as a unique tracer for vegetative burning smoke to allow for a better separation from other combustion sources. The average $PM_{2.5}$ contribution from airborne soil was 4.6 μg m^{-3} (38%); from vegetative burning 4.0 μg m^{-3} (35%); from sulfate aerosol 2.2 μg m^{-3} (20%); from vehicular traffic 0.2 μg m^{-3} (2%); from cooking 0.1 μg m^{-3} (1%); and 0.4 μg m^{-3} (4%) from unexplained sources. Table 5 summarizes the average source contributions to fine aerosol mass concentrations in this study and compares our results with those from a source apportionment study in Spokane (Kim et al., 2003), which is a larger city approximately 120 Kilometers north of Pullman. The average CMB vegetative burning $PM_{2.5}$ was slightly higher in Spokane than Pullman. However, the average airborne soil $PM_{2.5}$ observed in Pullman was four times larger than that in Spokane. This is probably due to the numerous unpaved roads surrounding Pullman. In addition, the contribution of $PM_{2.5}$ from vehicles was greater in Spokane than in Pullman, which is consistent with the greater amount of vehicular traffic in Spokane. The average contribution of sulfate aerosol to $PM_{2.5}$ was similar in both cites, suggesting a regional source of sulfate aerosol. During the study we found a significant inverse correlation (r= -

0.6, $p < 0.01$) between LG and ambient temperature, which could be due to limited atmospheric mixing or more frequent residential wood burning at lower temperatures. Note that we could not distinguish LG emitted from residential wood burning from that emitted by agricultural burning.

PMF modeling results

The 3-source PMF model identified vegetative burning, windblown dust, and secondary sulfate sources, with similar source profiles (shown as grey bars in Figure 2) to those used in the CMB analysis. This suggests that the CMB source profiles, which were compiled from studies in nearby cities, were suitable for the Pullman airshed. Note that LG was a significant component in only one profile (vegetative burning) in the PMF modeling results, supporting the use of LG as a unique tracer for vegetative burning. The source-specific $PM_{2.5}$ mass concentrations estimated from the two models (PMF and CMB) were highly correlated ($p<0.01$), with a Pearson's correlation coefficient of 0.70, 1.00, and 0.88 for vegetative burning, windblown dust, and secondary sulfate contributions respectively (Figure 3). However, when compared to CMB estimates, the PMF apportioned $PM_{2.5}$ mass concentrations were consistently lower (~46% lower) for vegetative burning and higher for airborne soil (~40% higher) and sulfate aerosol (~70% higher). This discrepancy could be explained by the slight differences in the relative proportion of tracers in source profiles resulting from literature values (CMB) and statistics (PMF). For further analysis, we chose the CMB estimates over the 3-source PMF results due to the sample size constraints for PMF (relatively small size N=123) (Henry, 2002). Ultimately, the PMF results served as an independent method to further

confirm the CMB results through the similarity of source profiles, identification of LG as a unique tracer for biomass burning, and high correlations of source estimates between the two methods.

2.3.3. Episode calls

Table 6 compares pollutant concentrations during episodes (16.8 ±8.6 μg m^{-3}) vs. non-episode days (10.5 ±8.5 μg m^{-3}), including the sham episode (4.9 ±4.0 μg m^{-3}). By definition, the continuous PM observations from the nephelometer were higher during all episodes than those during non-episode days. LG, NO_x, CO_2, and OC were also higher during episode than non-episode days, with or without controlling for temperature using ANOVA. The CMB-estimated source contributions for episode vs. non-episode days are also shown in Table 6. PM from vegetative burning was significantly higher during episode days (5.2 μg m^{-3}) than non-episode days (3.0 μg m^{-3}). However, we found a larger contribution of $PM_{2.5}$ from soil during episode (6.9 μg m^{-3}) than non-episode days (2.8 μg m^{-3}). As expected, PM from other sources (secondary sulfate, vehicle, and cooking) did not differ between episodes and non-episode days.

This study was conducted during the fall dry season, which also experienced enhanced dust intrusion from nearby roads and adjacent fields upwind of Pullman. Thus, it was likely that the real-time $PM_{2.5}$ measurements were enhanced by both the presence of airborne soil dust and vegetative burning smoke. Although if an episode declaration was based solely on the criterion of exceeding a threshold $PM_{2.5}$ value of 40 μg m^{-3}, the mass measurements alone could not distinguish the soil from the biomass burning contribution. We also analyzed the effects of burn calls and total acreage burned during

episode vs. non-episode days. These attempts failed because of the difficulties in collecting burn calls in the region across two states and inaccurate records of acreages burned. We also conducted back trajectory analyses to track movement of the air mass during episodes, but encountered similar difficulties in locating the exact field burn sites on any specific day.

2.4 CONCLUSIONS

This study characterized the air quality in Pullman during the 2002 fall burning season. We found that the average $PM_{2.5}$, OC and EC concentrations in Pullman were very similar during the daytime and nighttime, while LG was significantly higher during the nighttime due to trapping inversions and/or possibly residential wood burning. Good correlations between $PM_{2.5}$ and NOx as well as with OC, LG and $HI_{2.5}$ suggested that some of the observed $PM_{2.5}$ originated from combustion sources upwind of the monitoring site.

Vegetative burning was found to be the second largest source of $PM_{2.5}$ (35%), after airborne soil (38%). Our CMB results were consistent with those found previously in Spokane. In addition, the a priori CMB source profiles were similar to those identified by the PMF algorithm. Furthermore, the source-specific $PM_{2.5}$ mass concentrations estimated by CMB were highly correlated with the contributions from the subset of sources identified by PMF. The PMF results confirmed that the CMB source profiles compiled from studies in other nearby cities were applicable to the Pullman airshed.

In this study, four smoke episodes were identified. LG, NO_x, CO_2, OC, and apportioned biomass burning $PM_{2.5}$ were higher during episode compared to non-episode

days. EC was not considerably elevated during the episode periods. On the other hand, airborne dust also showed elevated levels during the defined field burning episodes. $PM_{2.5}$ measurements alone could not be used to distinguish biomass combustion contribution from soil contribution during these episodes because the study was conducted in the dry season with soil enhancement.

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(*Tables and Figures follow references*)

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Table 1

Historical $PM_{2.5}$ hourly nephelometer measurements at the near downtown Pullman monitoring site operated by the Washington State Department of Ecology.

	September - October		
Range of $PM_{2.5}$	Year 2000 Frequency	Year 2001 Frequency	Year 2002 Frequency
$0 < PM_{2.5} < 10$ µg/m^3	1113	992	753
$10 < PM_{2.5} < 40$ µg/m^3	332	117	635
$PM_{2.5} > 40$ µg/m^3	13	4	4

Table 2

Summary of statistics for PM and gaseous pollutant observations at the central site during the two-month study period.

Parameter	$TEOM_{10}$ (µg/m^3)	$TEOM_{2.5}$ (µg/m^3)	Neph $PM_{2.5}$ (µg/m^3)	CO (ppm)	NOx (ppb)	CO_2 (ppm)
Mean	40.5	13.6	11.3	0.51	34.9	465
Standard Deviation	38.8	9.4	8.0	0.56	38.1	29
25 percentile	16.2	6.8	4.9	0.09	9.8	438
Median	28.6	11.4	9.3	0.32	20.1	464
75 percentile	51.9	17.8	15.9	0.71	45.5	483
Observations (N)	2684	1872	2788	784	2857	2841
Frequency $PM_{2.5} > 40$ µg/m^3	-	38	9	-	-	-

30-minutes average integration time

Table 3

Summary of statistics for the 12-hour integrated $PM_{2.5}$ samples at the central site during the two-month study period.

	Day					Night				
Species	Mean	Median	Min	Max	N	Mean	Median	Min	Max	N
[1]$HI_{2.5}$ $^{++}$	10.0	9.6	2.9	21.9	58	13.0	11.3	2.1	31.0	59
[1]OC	3.8	3.6	1.1	7.1	56	3.9	3.77	1.0	7.8	57
[1]EC	0.4	0.2	0.0	3.3	56	0.5	0.4	0.0	1.9	57
[2]LG $^{++}$	50	31	2	327	45	96	76	3	318	50
[2]Si $^{++}$	413	361	20	2088	60	996	967	13	2721	63
[2]Al $^{++}$	137	121	0	692	60	363	313	0	958	63
[2]S $^{++}$	252	252	68	675	60	206	177	62	416	63
[2]Ca $^{++}$	77	71	4	333	60	210	148	0	533	63
[2]K $^{++}$	83	71	19	254	60	121	118	13	287	63
[2]Na	46	30	0	315	60	52	20	0	272	63
[2]Mg $^{++}$	12	3	0	87	60	38	19	0	186	63
[2]Ba	6	0	0	44	60	8	0	0	64	63
[2]Zn $^{+}$	6	4	0	28	60	8	6	0	31	63
[2]Cl	6	2	0	72	60	7	4	0	45	63

[1]Units of mass concentration in $\mu g/m^3$ [2]Units of mass concentration in ng/m^3

$^{++}p< 0.01$; $^{+}p< 0.05$

Table 4

Summary of correlation coefficients between PM, NOx, CO_2, EC, OC and levoglucosan (LG) observed during the study.

	Spearman's correlation coefficients								
	$TEOM_{10}$	$TEOM_{2.5}$	Neph $PM_{2.5}$	$HI_{2.5}$	CO_2	NOx	OC	EC	LG
$TEOM_{10}$	1	0.85^{++}	0.60^{++}	0.76^{++}	0.24^{++}	0.42^{++}	0.37^{++}	0.41^{++}	0.17
$TEOM_{2.5}$	0.84^{++} (1699)	1	0.77^{++}	0.79^{++}	0.17^{++}	0.49^{++}	0.49^{++}	0.49^{++}	0.35
Neph $PM_{2.5}$	0.50^{++} (2607)	0.71^{++} (1634)	1	0.79^{++}	0.13^{++}	0.44^{++}	0.64^{++}	0.48^{++}	0.56^{++}
$HI_{2.5}$	0.76^{++} (116)	0.82^{++} (70)	0.81^{++} (110)	1	0.02	0.52^{++}	0.63^{++}	0.54^{++}	0.42^{++}
CO_2	0.22^{++} (2585)	0.23^{++} (1730)	0.16^{++} (2548)	0.06 (116)	1	0.32^{++}	-0.02	-0.06	0.25^{+}
NOx	0.38^{++} (2588)	0.48^{++} (1732)	0.41^{++} (2550)	0.53^{++} (116)	0.30^{++} (2765)	1	0.25^{++}	0.56^{++}	0.29^{++}
OC	0.29^{++} (118)	0.45^{++} (81)	0.61^{++} (116)	0.64^{++} (104)	-0.07 (118)	0.24^{++} (118)	1	0.50^{++}	0.44^{++}
EC	0.31^{++} (118)	0.36^{++} (81)	0.40^{++} (116)	0.42^{++} (116)	-0.1 (117)	0.47^{++} (118)	0.41^{++} (118)	1	0.41^{++}
LG	0.16 (95)	0.30^{+} (62)	0.61^{++} (93)	0.47^{++} (94)	-0.13 (94)	0.25^{+} (95)	0.47^{++} (95)	0.18 (95)	1
	Pearson's correlation coefficients								

$^{++}p< 0.01$; $^{+}p< 0.05$; (N)

Table 5

Summary of average source contributions to fine particle mass concentration found in Spokane and Pullman.

Average source contribution in Spokane *Kim et al. (2003)			Average source contribution in Pullman				
Mass contribution	PMF			CMB		**PMF	
	($\mu g/m^3$)	%		($\mu g/m^3$)	%	($\mu g/m^3$)	%
Vegetative burning	5.28 ±0.14	44	Vegetative burning	3.96 ±0.13	35	1.81 ±1.57	17
Airborne soil	1.01 ±0.04	8	Airborne soil	4.55 ±0.03	38	6.20 ±5.22	57
Sulfate aerosol	2.30 ±0.04	19	Sulfate aerosol	2.22 ±0.06	20	2.82 ±2.14	26
Motor vehicle	1.29 ±0.04	11	Motor vehicle	0.19 ±0.01	2	-	-
Nitrate aerosol	1.04 ±0.05	9	Cooking	0.12 ±0.04	1	-	-
Chlorine-rich	0.68 ±0.03	6	Unexplained	0.42 ±0.24	4	-	-
Metal processing	0.29 ±0.01	3					

*The Spokane study was conducted from 1995 through 1997, and PMF was used for source apportionment

**PMF estimates and standard deviation, (N=123).

Table 6

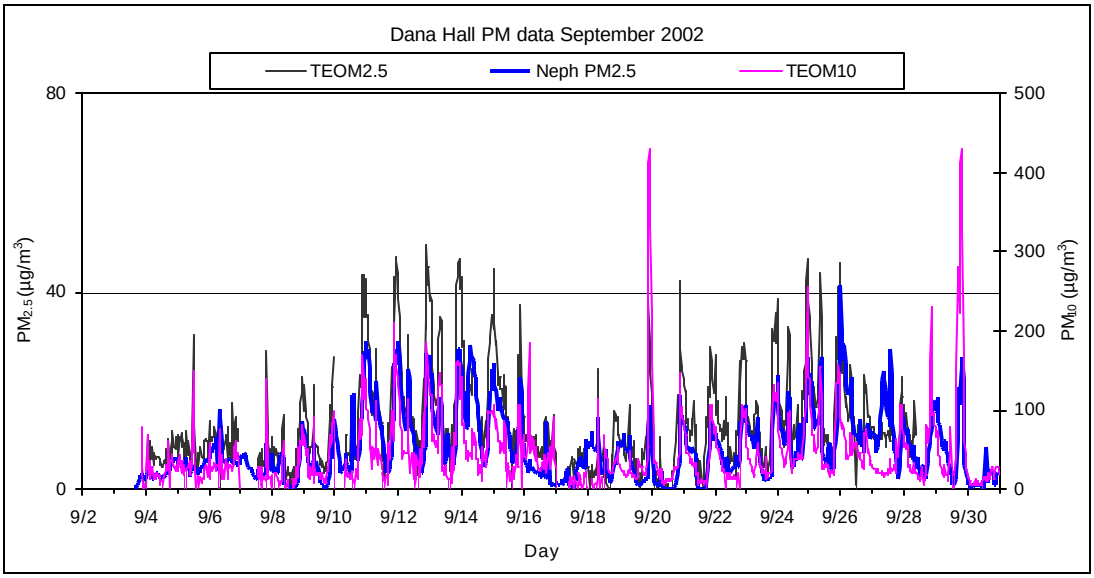
Summary of results comparing (t-test[*]) air pollution measurements and estimates between real episode (regardless of declaration) and non-episode (including sham) days.

Variable	All episodes [**]Mean ±SD (N)	Non episodes [**]Mean ±SD (N)
Neph $PM_{2.5}$ ($\mu g/m^3$)	16.76 8.63 (1442)	10.30 8.79 (7119)
LG (ng/m^3)	106 115 (19)	59 70 (86)
NO_x (ppb)	42.33 43.31 (461)	33.94 37.01 (2370)
CO_2 (ppm)	470 36 (483)	463 30 (2362)
OC ($\mu g/m^3$)	4.75 1.94[++] (24)	3.14 1.48 (94)
EC ($\mu g/m^3$)	0.59 0.53[++] (24)	0.41 0.53 (94)
Vegetative burning ($\mu g/m^3$)	5.22 2.96[++] (19)	2.97 1.80 (78)
Airborne soil ($\mu g/m^3$)	6.92 3.86 (19)	2.83 2.73 (78)
Sulfate ($\mu g/m^3$)	2.41 0.75[++] (19)	2.21 1.13 (78)
Vehicles ($\mu g/m^3$)	0.22 0.19[++] (19)	0.15 0.17 (78)
Cooking ($\mu g/m^3$)	0.09 0.19 (19)	0.11 0.29 (78)

[*]t-test applied to normally or log-normal distributed data

[**]original data

[++]$p< 0.01$; [+]$p< 0.05$



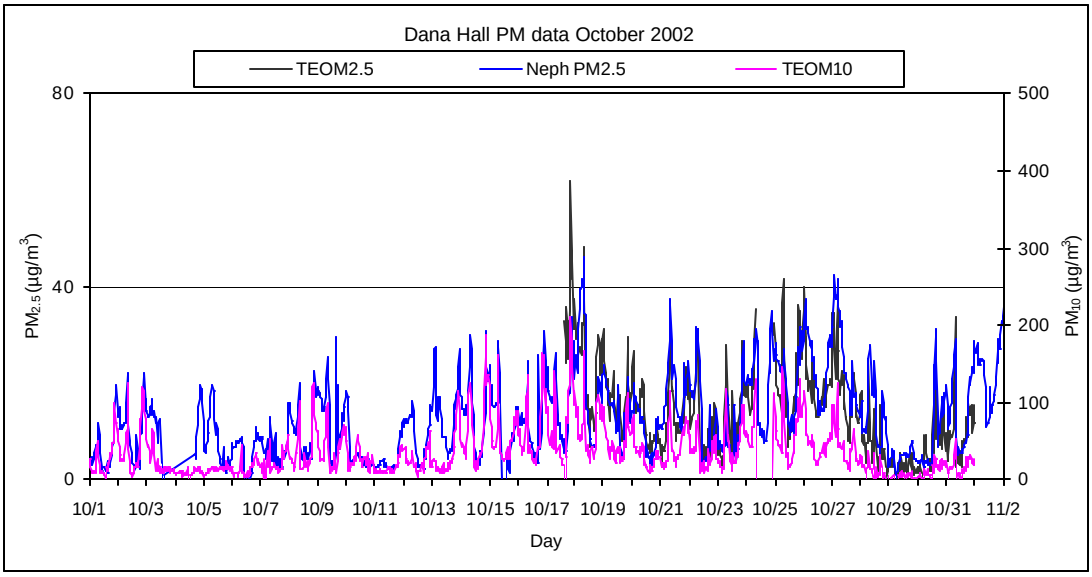


Figure 1. Continuous 30-min average $PM_{2.5}$ and PM_{10} concentrations measured by TEOM and nephelometer.

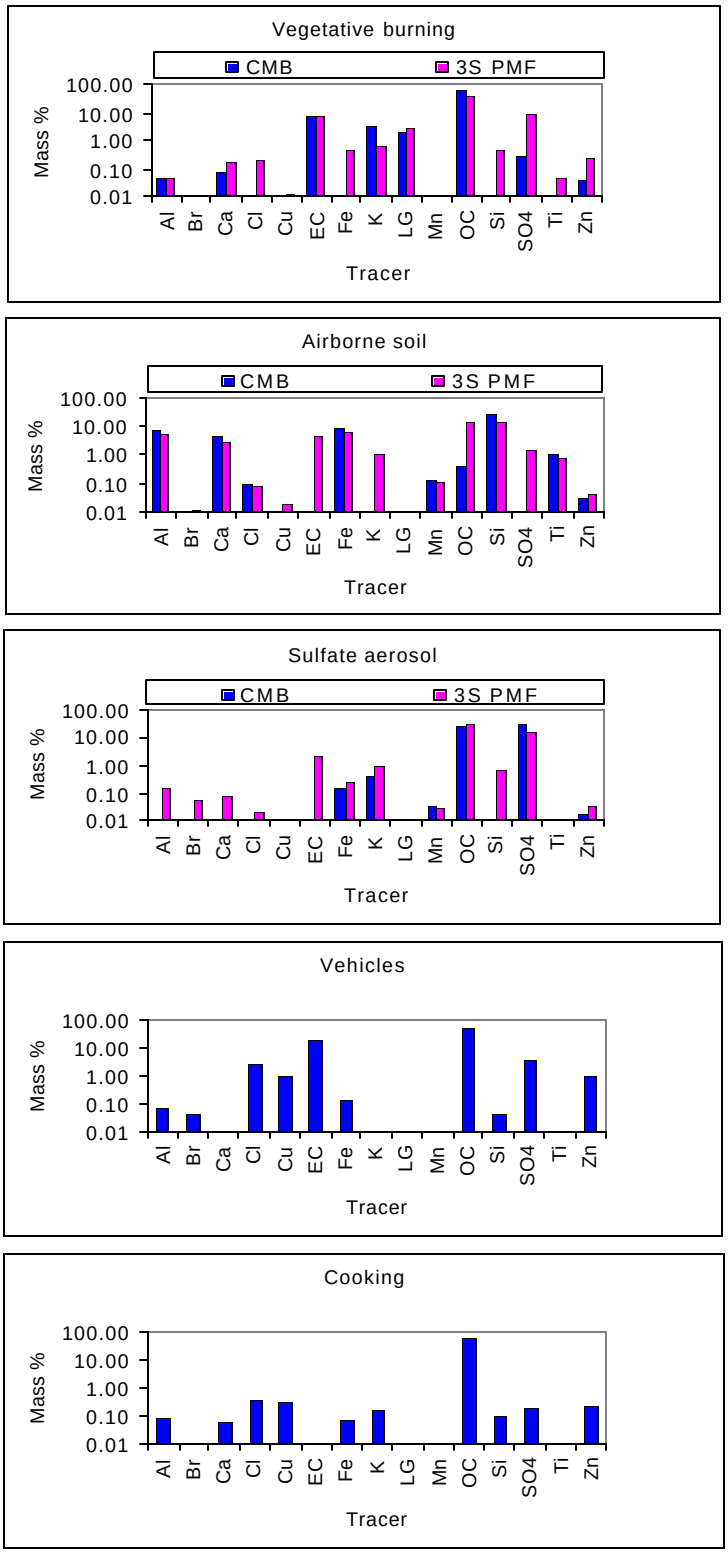
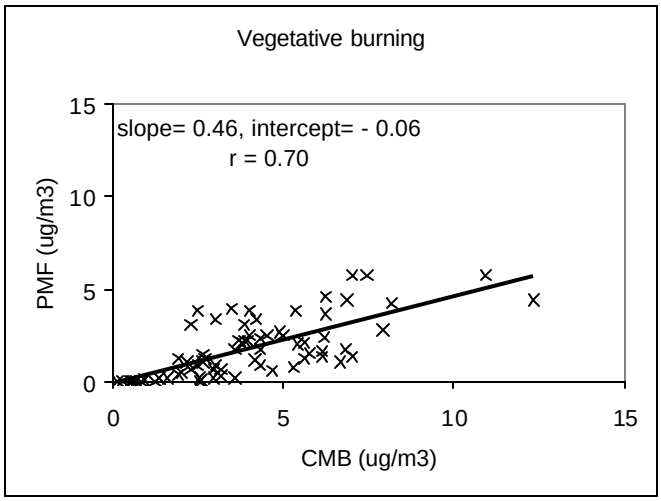
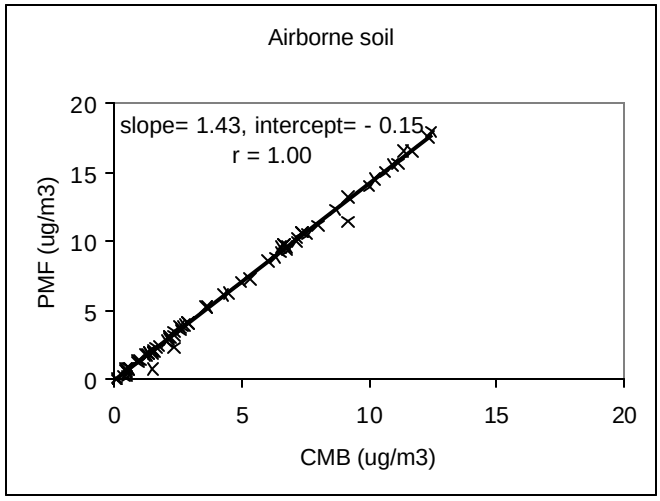


Figure 2. Source profiles selected for CMB and predicted by 3s PMF analysis for the samples collected at the central site in Pullman during the two month study.





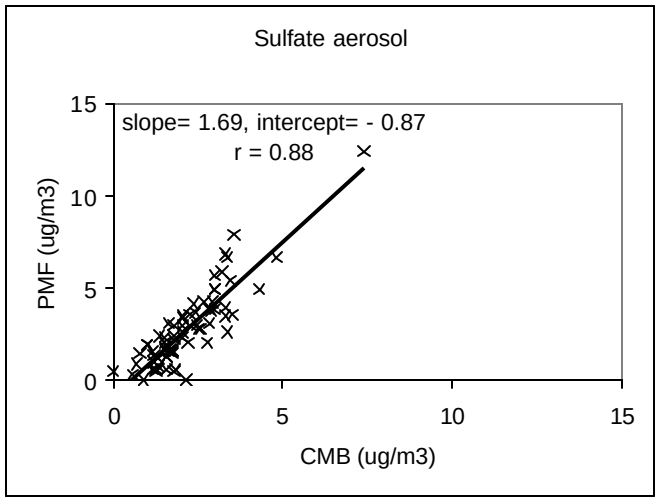


Figure 3. Correlation between CMB and PMF 3S apportionment for the major sources of fine PM in Pullman.

Chapter 3

Developing a Source Fingerprint for Burning of Wheat and Kentucky Bluegrass Stubble in Eastern Washington and Northern Idaho

Developing a Source Fingerprint for Burning of Wheat and Kentucky Bluegrass Stubble in Eastern Washington and Northern Idaho

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ABSTRACT

Air quality in eastern Washington is compromised by various pollution sources, of which agricultural field burning smoke is a particular concern. Large amounts of particulate matter are released into the air in a relatively short period of time when agricultural residues of wheat and Kentucky bluegrass (KBG) are burned. Smoke from field burning is a nuisance to nearby communities and is a concern for health reasons. The purpose of this study was to evaluate levoglucosan and lignin pyrolysis products as potential tracers for apportioning PM pollution from wheat and KBG stubble smoke. $PM_{2.5}$ (particulate matter less than 2.5 µm in aerodynamic diameter) samples from wheat and KBG stubble smoke were collected from controlled chamber burns, as well as from field burns in the region. These were analyzed for inorganic and organic compounds, including levoglucosan (LG) and 19 methoxyphenols (MPs). For the chamber experiments, the amount of LG, ~23 µg mg^{-1} of $PM_{2.5}$, found in wheat and KBG stubble smoke was relatively similar, while the amount of total MPs was higher in wheat stubble smoke compared to the KBG smoke. In the field, the amount of LG present in wheat stubble smoke was ~78 µg mg^{-1} of $PM_{2.5}$, approximately four times higher than the levels found in the chamber. Trace elements associated with soil minerals (Si, AL, Fe, Ca) were found in smoke samples collected from wheat stubble burning in the field. Syringaldehyde, acetosyringone and coniferylaldehyde were found to be the most prominent particle-phase MPs in wheat smoke, and these compounds were not always present in detectable amounts in KBG smoke. The ratio of LG/ syringaldehyde found in wheat (~80) was much higher than the same ratio reported for hardwood (~5). Softwoods have a lower LG/ coniferylaldehyde ratio (~7) compared to wheat stubble smoke (~180).

3.1 INTRODUCTION

In the past decade, agricultural field burning has been the subject of analysis and public debate in eastern Washington and northern Idaho. As wheat and Kentucky bluegrass (KGB) farmers prepare their fields for seeding, some of their practices involve the use of fire, and citizens have voiced health concerns related to smoke exposure, as well as potentially negative impacts on tourism and economic activities in the area (Roberts and Corkill, 1998; Jimenez 2002).

Biomass smoke includes both vapor and particulate phase material, with much of the particulate matter (PM) in the $PM_{2.5}$ (PM less than 2.5 μm in aerodynamic diameter) size range. PM in biomass burning smoke can have a potentially detrimental impact on human health from both chronic and acute exposures. Chronic exposure to biomass smoke could reduce lung function, depress the immune system, and increase the risk of respiratory diseases (Long et al., 1998; Sutherland and Martin, 2003; Sutherland, 2004). Short-term exposure to high levels of $PM_{2.5}$ result in acute health effects in susceptible people, including chronic obstructive pulmonary disease (COPD) patients, and asthmatic children (Romieu et al., 1996; Pekkanen et al., 1997; Peters et al., 1997). Clearly, as the population in eastern Washington and northern Idaho continues to grow, there is a need for an improved understanding of the extent of air pollution from agricultural field burning in the region.

In addition to smoke from agricultural field burning, eastern Washington, a semi-arid region, can have significant levels of PM from a variety of sources. These sources include fugitive dust from roads and fields (Claiborn et al., 2000; Kim et al., 2003, Jimenez et al., 2006), and regional forest fires (Jimenez, 2002). Receptor models can be

used for identifying and apportioning smoke from agricultural field burning among other sources of PM affecting the region. They use chemical and physical characteristics of PM to both identify and quantify source contributions at any given location (Schauer et al., 1996; Turn, 1997; Schauer et al., 2000; Jimenez et al., 2006). This technique can be used to apportion air pollution from field burning in the populated areas of eastern Washington and northern Idaho.

Major compound groups identified in smoke particles emitted during biomass combustion of several plant species have been reported elsewhere (Hawthorne et al., 1988; Edye and Richards, 1991; Oros and Simoneit, 1999, Oros and Simoneit, 2001; Fine et al., 2001; Fine et al., 2002; Sheesley et al., 2003; Hays et al., 2005). They consist of natural and combustion alteration products, whose emissions vary by plant species. These compounds include homologous series of n-alkanes, n-alkenes, n-alkanoic acids and n-alkanols; methoxyphenolics from lignin, monosaccharide derivates from cellulose, steroids and terpenoids markers and polycyclic aromatic hydrocarbons (PAHs).

Cellulose pyrolysis yields tarry anhydro sugars and volatile organic compounds, which includes the molecular tracer 1,6-anhydro-β-D-glucopyranose, commonly known as levoglucosan (LG). LG has been reported to be present in the particle-phase in measurable amounts and is relatively stable in the atmosphere showing no decay over 8 hours of exposure to ambient conditions and sunlight (Simoneit, 2002). In addition, lignin pyrolysis products are important compounds in smoke samples from biomass combustion (Simoneit et al, 2000). The relative proportion of some of these has been used to distinguish wood smoke derived from hardwood versus softwood combustion. It is possible that similar diagnostic ratios may be used to distinguish residential wood

combustion from agricultural burning smoke or to identify PM from combustion of wheat and bluegrass stubble. However, relative emissions of organic tracers for smoke from these crop residues have not been thoroughly reported in the literature.

The objectives of this research were to identify and quantify emissions and relative proportions of trace compounds present in smoke from combustion of wheat and bluegrass stubble in eastern Washington and northern Idaho and to evaluate levoglucosan and 19 methoxyphenols (MPs) as potential tracers for characterizing wheat and KBG stubble smoke. For this purpose we collected and analyzed $PM_{2.5}$ samples from wheat and KBG stubble smoke from controlled conditions (chamber), as well as from prescribed field burns in the region. In addition, this study compares the experimentally determined profiles with profiles used in a recent source apportionment study in Pullman, WA (Jimenez et al., 2006).

3.2 METHODS

Wheat (*Triticum aestivum L.*, variety Madsen) and KBG (*Poa pratensis L.*) stubble were burned under controlled (chamber experiments) and real world conditions (field experiments), for the purpose of obtaining $PM_{2.5}$ samples for analysis and identification of selected organic and inorganic tracers. Chamber experiments were conducted in the summer of 2004 at the EPA test burn facility located at the Research Triangle Park, North Carolina. The wheat or bluegrass stubble was oriented as near as possible to that found in the field during the burn (~0.8 kg per burn). The burn's flaming stage typically lasted 1-2 min and was followed by a smoldering stage of approximately 15 min (see Dhammapala et al., 2006 for more details).

Field samples from wheat and KBG stubble burns were collected during the fall of 2004 and spring of 2005. $PM_{2.5}$ samples were collected from samplers deployed at the edge of the field at ground level, downwind of the fire.

3.2.1. Particle collection and analysis

$PM_{2.5}$ samples were collected using collocated 5 L min^{-1} low volume (LowVols) samplers (Air Metrics Inc., Eugene, OR) equipped with single-stage inertial $PM_{2.5}$ inlets. Two LowVols sampled $PM_{2.5}$ onto 47-mm Teflon filters (2 µm pore size, cat. No 7592-104, Whatman Inc., Clifton, NJ), one with a quartz filter (cat. No 1851047, Whatman Inc., Clifton, NJ) after the Teflon, and a third sampler collected $PM_{2.5}$ onto a quartz filter. Field experiments included a similar set of samples collected upwind of the burning area to correct for pre-existing (background) conditions. A similar correction was applied to the smoke samples collected in the chamber experiments from a blank run (no fire involved), which was done at the end of the cycle of burns. In addition, polyurethane foam (PUF) sheets were used behind Teflon filters to collect vapor-phase organic compounds including polycyclic aromatic hydrocarbons (PAHs) and methoxyphenols (MPs). The results of this analysis are reported in Dhammapala et al. (2006a, 2006b).

$PM_{2.5}$ collected on the Teflon media was analyzed gravimetrically to determine $PM_{2.5}$ concentration by using a microbalance (model C-34, Cahn Instruments, CA, USA). Filters were equilibrated at a constant temperature (24±2^{o}C) and relative humidity (50±5%) for at least 24 hours prior to weighing (Allen et al., 2001). In addition, Teflon filters were analyzed for 55 elements using X-Ray Fluorescence (XRF) (Chester LabNet, Tigard, Oregon). Sections of the PM collected on quartz filters (1.5 cm^2) were analyzed

for organic carbon (OC) and elemental carbon (EC) via Thermal Optical Transmittance (TOT) (Sunset Laboratory, Inc. Tigard, OR) using a modified version of the NIOSH 5040 method (Pang et al., 2002) to determine the carbonaceous fractions of the $PM_{2.5}$ collected from smoke. The duplicate Teflon filters were extracted by ultrasonication in ethylacetate containing 0.5% (v/v) triethylamine and analyzed for LG and 19 MPs using Gas Chromatography - Mass Spectrometry (GC-MS). The GC-MS was operated in selective ion monitoring mode (refer to Simpson et al., 2004 and Simpson et al., 2005 for more details about the method). Samples were also analyzed for PAHs and the results are reported elsewhere (Dhammapala et al., 2006b).

3.2.2. Quality assurance

The results of the analysis (gravimetric, TOT, XRF and GC-MS) of the $PM_{2.5}$ samples from smoke were subject to blank corrections and consistency checks with duplicates to determine uncertainties associated with measurements. Quartz filters were pre-heated at 800 ^{o}C for at least 8 hours to eliminate any contamination prior to PM collection. Artifact corrections were applied to account for vapor-phase OC (SVOC) absorbed into the quartz filter. This correction was done by subtracting the back (after Teflon) quartz filter OC from the OC obtained from the single quartz filter (Fitz, 1990; Turpin et al., 1994). Blank filters were extracted with each batch of samples. Analyte levels in extracts from blank filters were either below detection limits, or were well below analyte levels measured in the samples.

Reconstructed fine mass [RCFM: defined as the sum of the individual components of fine PM from each chemical analysis; i.e. OC, EC and inorganic elements

(Malm et al., 1994)] was calculated from the chemical composition analysis and compared to $PM_{2.5}$ concentration estimated gravimetrically to determine if the composition information explains the total $PM_{2.5}$ collected in each set of experiments.

3.3 RESULTS AND DISCUSSIONS

3.3.1. Chamber experiments

The breakdown of the major constituents of $PM_{2.5}$ from smoke of KBG and wheat in the chamber experiments is shown in Figure 1. OC mass was converted to particulate organic matter (POM) by multiplying by a factor that accounts for hydrogen, oxygen and some nitrogen content present in the organics. Values of 1.2 to 1.4 have been reported for atmospheric aerosols (Gray et al., 1986; Malm et al., 1994), and may be higher depending on the amount of oxygenated organic compounds present in the sample (Fine et al., 2001). In our analysis, we consider a scale factor of 1.4 to convert the measured OC to POM. The reconstructed mass (POM+EC+metals) obtained from the ensemble of analyses was compared to the $PM_{2.5}$ determined gravimetrically. Figure 1 illustrates this comparison for the smoke PM samples collected in the chamber, where 71±19% (KBG) and 100±14% (wheat) of the $PM_{2.5}$ mass were explained by the RCFM approach.

The relative emissions of OC, EC, and trace elements from the combustion of wheat and KBG stubble in the chamber experiments are listed in Table 1. The $PM_{2.5}$ emission factors were 3.0±0.6 g kg^{-1} of fuel for wheat, and 12.1±1.4 g kg^{-1} of fuel for KBG burned in the chamber. For more details about PAHs and MPs emission factors and combustion efficiencies refer to Dhammapala et al. (2006). These emission factors of $PM_{2.5}$ were relatively similar to those documented for hardwood and softwood

combustion of selected species commonly used in fireplaces in the eastern U.S. (Fine et al., 2001; 2002). In addition, the results listed in Table 1 indicate that the majority of the $PM_{2.5}$ mass found in the smoke was made of organic compounds (OC) (POM ~64% wheat and ~52% for KBG, respectively), followed by EC, potassium (K), and chlorine (Cl). Potassium, commonly used as a tracer for biomass burning (Echalar et al., 1995), was found to be approximately 10 wt% of the total $PM_{2.5}$ from wheat stubble smoke and 6 wt% for KBG in the chamber experiments.

The relative amounts of the selected organic markers found in wheat and KBG stubble smoke in the chamber experiments are listed in Table 2. LG was the most abundant of the analyzed organic compounds accounting for ~2% of the $PM_{2.5}$ mass emitted during the combustion of the stubble, and was slightly higher in KBG compared to wheat stubble smoke. These values were consistent with a similar study reporting values of LG for wheat residue smoke (see Table 5, Hays et al., 2005), but were much lower than the LG content found in smoke from hardwood combustion (Fine et al., 2001; 2002). In addition, the amounts of MPs were much higher in $PM_{2.5}$ from wheat stubble smoke (6.3±2.7 μg mg^{-1} $PM_{2.5}$) compared to the KBG smoke (1.0±0.5 μg mg^{-1} $PM_{2.5}$), and were much lower than similar groups of compounds found in smoke from hardwood burning (~20-80 μg mg^{-1} $PM_{2.5}$, Fine et al., 2001; 2002).

3.3.2. Field experiments

Figure 2 shows the breakdown of the major constituents of $PM_{2.5}$ found in wheat and KBG stubble smoke collected in the field. The $PM_{2.5}$ emission factors in the field were 8.3±4.4 g kg^{-1} fuel for wheat and 22.4±0.2 g kg^{-1} fuel for KBG stubble burning [refer to Dhammapala et al. (2006b) for more details about emission factor calculations for the field]. The RCFM for the $PM_{2.5}$ field samples explained 54±12% for wheat and 36±16% for KBG stubble burning, which were lower than the explained mass for the $PM_{2.5}$ samples collected in the chamber experiments (Figure 1). Note that the $PM_{2.5}$ samples collected from field burning of KBG were not analyzed for inorganic tracers (see Figure 2), but the low percent of mass explained for the $PM_{2.5}$ samples from KBG stubble smoke is not likely to be caused solely by the missing inorganic mass information. The sum of all analyzed inorganic tracers for wheat smoke were less than 3 %wt of the $PM_{2.5}$ mass collected in the field. In the chamber experiments the amounts of metals present in smoke from KBG stubble were lower than the amount found in wheat stubble smoke (Table 1).

The emissions of EC, OC, and trace metals found in stubble smoke collected in the field are summarized in Table 3. Like the $PM_{2.5}$ smoke samples collected in the chamber experiments, the $PM_{2.5}$ smoke samples from the field mainly consisted of organic compounds (POM ~47% wheat and ~33% for KBG, respectively). The amounts of potassium (7.5±1.4 µg mg^{-1} $PM_{2.5}$), and chloride (2.4±1.1 µg mg^{-1} $PM_{2.5}$) were more than ten times lower (<1 wt%) in the field for wheat than similar parameters measured in the chamber experiments (see Table 1). Furthermore, trace elements predominantly associated with soil (Malm et al., 1994), were found in the smoke samples collected from

wheat stubble smoke in the field. Small amounts of silicon (Si), calcium (Ca), iron (Fe), and aluminum (Al) indicate that soil material (with less than 3% contribution to the total observed $PM_{2.5}$) may be suspended by the buoyancy of the fire and/or the farming equipment working in the field during the prescribed burn.

The selected organic markers for wheat and KBG stubble combustion in the field are listed in Table 4. LG was also the most abundant organic compound measured, accounting for ~8% of the $PM_{2.5}$ mass collected from wheat stubble smoke. The relative amounts of LG in the field were higher than those measured in the chamber experiment for wheat combustion. Conversely, the emission of LG from KBG in the field was less than 1% of the total $PM_{2.5}$ mass in smoke.

For KBG burning, the higher emissions of LG found in the chamber smoke samples compared to field samples could be due to the condition of residue combusted. The residual plant material combusted in the KBG fields (non-irrigated) were mainly scattered patches of short stubble and newly growing grass, which smoldered without a vigorous flame. In the chamber experiments, the KBG material combusted was mainly the excess of residue removed from the field (irrigated fields), which included more stems and woody plant material.

The amount of MPs in the $PM_{2.5}$ samples collected in the field was also higher in wheat stubble smoke (3.2±0.6 μg mg^{-1} $PM_{2.5}$) compared to the KBG smoke (0.9±0.2 μg mg^{-1} $PM_{2.5}$). However, the relative proportion of the MPs found in the field samples collected from wheat were lower than similar compounds measured in $PM_{2.5}$ samples in the chamber, with the exception of two syringol compounds (syringaldehyde and acetosyringone) that were higher in the field samples compared to chamber samples. The

lower relative proportions of the methoxyphenols in smoke collected in the field compared to the chamber experiments were not anticipated. One possible explanation may be enhanced volatilization of methoxyphenols from particles in the field experiment.

Additionally, photochemical degradation and transformation of methoxyphenols has been previously reported (Hawthorne et al., 1992). In a study in Minneaplois, MN, Hawthorne noted that the relative amounts of syringaldehyde and acetosyringone were enhanced in ambient PM samples compared to PM collected directly from fireplace chimneys. The authors speculated that this enhancement may de due to oxidative transformation of other syringyl-type MPs into syringaldehyde and acetosyringone. A similar mechanism may explain our observation of an apparent increase in the relative concentrations of syringaldehyde and acetosyringone in the field samples compared to the chamber samples, while relative concentrations of the other syringyl derivatives were reduced.

Coniferylaldehyde, syringaldehyde and acetosyringone were found to be the most prominent particle-phase tracers for wheat smoke among the methoxyphenols analyzed in this work. Reported values for OC, EC, LG and MPs content in smoke from combustion of different types of plant material are summarized in Table 5. In comparison with softwoods, hardwood smoke, such as red maple, is enriched with syringyl-type methoxyphenols. In addition, hardwood smoke contains higher amounts of levoglucosan, coniferylaldehyde, syringaldehyde and acetosyringone compared to the amounts found in wheat. However, the ratio of LG/ syringaldehyde found in wheat was much higher (~80, based on Table 4) than the same ratio reported for hardwood (~5) (Fine et al., 2001; Fine et al., 2002; Hays et al., 2002). Similarly, smoke from softwood has a low ratio (~7) of

LG/ coniferylaldehyde compared to wheat stubble smoke (~180, based on Table 4) due to its higher content of coniferylaldehyde in proportion to LG.

3.3.3. Profile comparison with previous work

Figure 3 shows the relative proportion of tracers found for wheat and KBG in this work, compared with the profiles selected for our previous source apportionments study in eastern Washington. The latter study was conducted in Pullman, WA during the prescribed field burning season of the fall 2002 (refer to Jimenez et al., 2006 for more details about the latter study). That particular study used a combination of two receptor models (CMB and PMF) to estimate smoke intrusions from agricultural field burning on the observed $PM_{2.5}$ mass concentrations. The modeling effort included a composite of vegetative burning smoke profile (CMB), and a statistically determined profile for regional field burning from Positive Matrix Factorization (PMF) modeling. Note from Figure 3 that the profiles for wheat and KBG determined in this work resemble the profiles used in this previous study, in particular, the relative proportion of LG, OC, EC, K, Cl, and S. In addition, the relative proportion of other trace metals, which are more predominant in the soil (Al, Ca, and Fe), also compared well for the profiles determined in the field. The inclusion of more specific types of organic tracers, such as lignin pyrolisis products, would further facilitate the characterization and apportionment of smoke from agricultural field burning in the region.

3.4 CONCLUSION

In this work, we identified and quantified emissions and relative proportions of trace elements and organic compounds present in $PM_{2.5}$ from smoke of wheat and Kentucky bluegrass crop residues in eastern Washington and northern Idaho. It was found from the chamber experiments that the relative amount of LG in $PM_{2.5}$ from wheat and KBG stubble smoke was similar (20 –25 μg mg^{-1} of $PM_{2.5}$), while the amount of total MPs was more than twice in wheat stubble smoke than in KBG smoke. The analyzed inorganic tracers in the chamber experiments were higher in $PM_{2.5}$ from wheat smoke compared with KBG smoke. Potassium and chlorine were predominant, and accounted for 18±4 % of the $PM_{2.5}$ mass in wheat smoke and 9±1% in KBG smoke. However, in the samples collected in the field during the spring, wheat stubble smoke exhibited a much lower contribution of inorganic tracers (<2% of $PM_{2.5}$ mass) and we did not have information regarding inorganic species present in field smoke from KBG stubble burning. Among the MPs analyzed in this work, syringaldehyde, acetosyringone and coniferylaldehyde were found to be the most prominent particle-phase tracers for wheat smoke, and these compounds were not always present in detectable amounts in KBG smoke. Additionally, the LG/ syringaldehyde ratio found in wheat was much higher than that reported for hardwood smoke, and the LG/ coniferylaldehyde ratio found in wheat stubble smoke was much higher than that reported for softwood smoke.

Finally, this work improves previous profiles for smoke from cereal crop waste that have been used in source apportionment studies in eastern Washington by including more specific types of organic tracers such as methoxyphenols. These profiles can be used in receptor models (CMB) to improve our current understanding of air quality

impacts from agricultural field burning in the populated areas of this region, and could provide substantial information for short and long-term studies on community exposure to pollution from agricultural field burning. This information could also help in developing future control strategies for field burning management and air quality improvement.

ACKNOWLEDGMENT

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(*Tables and Figures follow references*)

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Table 1

Summary of carbonaceous fractions and trace inorganic elements composition from combustion of wheat and Kentucky bluegrass (KBG) stubble in chamber experiments.

	Wheat	KBG
	Fine particulate matter emission factors, g $PM_{2.5}$ kg^{-1} fuel	
	3.0±0.6[a]	12.1±1.4[a]
	Units of µg mg^{-1} $PM_{2.5}$ ±SD	
Carbonaceous fractions	(N=3)	(N=4)
EC	142.0±25.1	67.4±34.5
OC	459.8±39.5	368.9±97.6
OC1	67.7±23.6	61.1±16.5
OC2	135.1±57.5	169.2±21.4
OC3	51.9±17.7	33.6±14.7
OC4	47.0±24.5	36.1±22.2
Pyro C	115.2±28.1	68.2±25.6
Trace elements[b]	(N=2)	(N=2)
Potassium	95.0±31.5	63.1±9.8
Chlorine	87.4±24.5	34.0±7.4
Sulfur	7.5±2.2	9.5±0.8
Sodium	5.5±0.1	2.3±1.3
Bromide	0.3±0.1	0.2±0.0

[a]For more detail about emission factor calculations refer to Dhammapala et al. (2006)

[b]The following elements were below detection or less than blanks; Mg, La, In, Fe, Cr, Zn, Zr, Ni, Al, Si, P, Ca, Ti, V, Mn, Co, Cu, Ga, Ge, As, Se, Rb, Sr, Y, Mo, Pd, Ag, Cd, Sn, Sb, Ba, Hg, Pb

N= number of samples; SD= standard deviation

Table 2

Summary of levoglucosan and methoxyphenols content in the $PM_{2.5}$ collected from smoke during combustion of wheat and Kentucky bluegrass (KBG) stubble in chamber experiments.

	Wheat		KBG	
	μg mg^{-1} $PM_{2.5}$ ±SD	μg mg^{-1} OC ±SD	μg mg^{-1} $PM_{2.5}$ ±SD	μg mg^{-1} OC ±SD
	(N=3)		(N=3)	
	Sugar derivatives			
Levoglucosan	19.95±6.50	43.38±14.61	25.96±18.67	70.37±53.93
	(N=4)		(N=4)	
	Guaiacol and substituted guaiacols			
Guaiacol	0.13±0.21	0.29±0.45	0.04±0.07	0.11±0.20
Eugenol	0.09±0.16	0.20±0.34	0.09±0.15	0.24±0.41
4-methylguaiacol	0.07±0.09	0.14±0.20	0.01±0.01	0.02±0.02
4-ethylguaiacol	0.19±0.32	0.41±0.70	0.03±0.04	0.07±0.12
4-propylguaiacol	0.06±0.09	0.14±0.19	0.02±0.03	0.05±0.09
Vanillin	0.14±0.04	0.31±0.10	0.24±0.27	0.65±0.73
Acetovanillone	0.28±0.46	0.62±1.01	0.08±0.10	0.22±0.28
Guaiacylacetone	0.58±0.93	1.25±2.02	0.14±0.22	0.38±0.61
Coniferylaldehyde	1.06±0.84	2.31±1.81	0.03±0.03	0.07±0.08
Sum guaiacyl compounds	2.61±1.40	5.67±3.05	0.67±0.40	1.81±1.12
	Syringol and substituted syringols			
Syringol	0.82±1.42	1.79±3.09	0.07±0.09	0.18±0.24
4-methylsyringol	0.47±0.81	1.03±1.76	0.11±0.17	0.30±0.47
4-ethylsyringol	1.10±1.54	2.39±3.35	0.03±0.02	0.07±0.06
4-Allylsyringol	0.26±0.35	0.58±0.76	0.10±0.14	0.26±0.38
4-propylsyringol	0.05±0.08	0.10±0.17	0.02±0.03	0.06±0.10
Syringaldehyde	0.46±0.26	0.99±0.57	ND	ND
Acetosyringone	0.38±0.37	0.82±0.80	ND	ND
Propylsyringone	0.09±0.11	0.20±0.24	0.03±0.01	0.07±0.02
Butylsyringone	0.02±0.03	0.05±0.07	<0.01	<0.01
Sinapylaldehyde	ND	ND	ND	ND
Sum syringyl compounds	3.66±2.32	7.96±5.06	0.28±0.24	0.95±0.66

N= number of samples; SD= standard deviation

ND= non detected or below blank values

Table 3

Summary of carbonaceous fractions and trace inorganic elements composition from combustion of wheat stubble in the field.

	Wheat	KBG
	Fine particulate matter emission factors, g $PM_{2.5}$ kg^{-1} fuel	
	8.3±4.4[a]	22.4±0.2[a]
	Units of μg mg^{-1} $PM_{2.5}$ ±SD	
Carbonaceous fractions	(N=6)	(N=2)
EC	20.0±11.7	34.2±15.0
OC	338.8±65.5	233.3±100.1
OC1	72.7±34.0	23.0±14.2
OC2	87.6±16.8	89.8±41.7
OC3	43.8±6.2	49.7±6.4
OC4	47.8±41.5	15.0±1.0
Pyro C	86.9±26.5	55.8±1.8
Trace elements[b]	(N=5)	(N=0)
Potassium	7.5±1.4	-
[c]Silicon	5.0±3.3	-
Chlorine	2.4±1.1	-
[c]Calcium	2.4±2.6	-
Sulfur	2.3±0.3	-
[c]Iron	1.9±1.1	-
Magnesium	1.1±0.7	-
[c]Aluminum	0.5±0.3	-

N= number of samples; SD= standard deviation

Trace elements not analyzed for $PM_{2.5}$ from KBG stubble burning in the field.

[a]For more detail about emission factor calculations refer to Dhammapala et al. (2006b)

[b]The following elements were below detection or less than blanks; Na, La, In, Br, Cr, Zn, Zr, Ni, P, Ti, V, Mn, Co, Cu, Ga, Ge, As, Se, Rb, Sr, Y, Mo, Pd, Ag, Cd, Sn, Sb, Ba, Hg, Pb.

[c]Elements predominately associated with soil.

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Table 4

Summary of levoglucosan and methoxyphenols content in the $PM_{2.5}$ collected from smoke during prescribed field burning of wheat and Kentucky bluegrass (KBG) in the region.

	Wheat		KBG	
	μg mg^{-1} $PM_{2.5}$ ±SD	μg mg^{-1} OC ±SD	μg mg^{-1} $PM_{2.5}$ ±SD	μg mg^{-1} OC ±SD
	(N=6)		(N=2)	
	Sugar derivatives			
Levoglucosan	77.79±11.29	229.59±55.49	7.88±5.96	33.77±29.37
	(N=6)		(N=2)	
	Guaiacol and substituted guaiacols			
Guaiacol	0.10±0.06	0.30±0.18	0.04±0.01	0.17±0.08
Eugenol	0.02±0.02	0.04±0.02	0.01±0.00	0.03±0.02
4-methylguaiacol	0.07±0.08	0.20±0.25	0.01±0.00	0.03±0.01
4-ethylguaiacol	0.02±0.02	0.06±0.06	ND	ND
4-propylguaiacol	ND	ND	ND	ND
Vanillin	0.12±0.03	0.35±0.12	0.19±0.11	0.79±0.57
Acetovanillone	0.06±0.04	0.17±0.13	0.01±0.00	0.03±0.02
Guaiacylacetone	0.10±0.07	0.29±0.20	0.01±0.00	0.03±0.02
Coniferylaldehyde	0.43±0.07	1.26±0.31	0.17±0.06	0.73±0.40
Sum guaiacyl compounds	0.90±0.15	2.67±0.52	0.44±0.12	1.81±0.70
	Syringol and substituted syringols			
Syringol	0.08±0.10	0.22±0.30	<0.01	0.01±0.01
4-methylsyringol	0.04±0.03	0.12±0.08	ND	ND
4-ethylsyringol	0.03±0.02	0.10±0.06	ND	ND
4-Allylsyringol	0.03±0.02	0.08±0.05	ND	ND
4-propylsyringol	0.03±0.04	0.08±0.10	ND	ND
Syringaldehyde	1.00±0.32	2.96±1.09	0.15±0.12	0.64±0.58
Acetosyringone	0.59±0.08	1.74±0.42	ND	ND
Propylsyringone	0.07±0.01	0.20±0.05	<0.01	0.02±0.01
Butylsyringone	ND	ND	ND	ND
Sinapylaldehyde	0.48±0.42	1.41±1.26	0.37±0.11	1.59±0.81
Sum syringyl compounds	2.34±0.54	6.90±1.75	0.52±0.16	2.26±1.00

N= number of samples; SD= standard deviation

ND= non detected or below blank values

Table 5

Summary of trace elements and organic compounds present in PM from smoke reported for several types of biomass fuels.

	Hays et al., 2005		Ward et al., 2006	Sheesley et al., 2003	Fine et al., 2001		Hays et al., 2002	
$\mu g\ mg^{-1}\ PM_{2.5}$	Wheat straw	Rice straw	Wildfires Missoula, MT	Rice straw	Red maple	Eastern white pine	Western hemlock	Foliar debris [a]
				Carbonaceous fractions				
OC	261.2±6.4	690.3±32.4	649.1±50.9	563±30	855±58	734±6	714.3±52.1	709.6
EC	110.4±0.8	13.1±3.1	62.1±18.9	11.0±2.2	67±19	313±28	35.7±9.2	14.7
				Sugar derivatives				
Levoglucosan	26.1±1.5	87.3±4.6	40.6±12.2	18.3±3.5	92.8±6.3	38.4±3.3	31.8±2.4	28.2
				Guaiacol and substituted guaiacols				
Guaiacol	0.01±0.00	0.03±0.00	N/A			0.05±0.00	0.02±0.01	0.03
Eugenol	<0.01	0.01±0.00	N/A		0.06±0.00	0.06±0.00	<0.01	0.02
4-methylguaiacol	N/A	N/A	N/A	0.060.01±	N/A	N/A	0.02±0.01	0.02
4-ethylguaiacol	<0.01	0.01±0.00	N/A	0.18±0.03	0.02±0.00	0.04±0.00	0.01±0.00	0.02
4-propylguaiacol	<0.01	<0.01	N/A			0.04±0.00	N/A	N/A
Vanillin	0.06±0.00	0.42±0.02	0.11±0.05	2.77±0.08		3.79±0.33	0.77±0.60	1.75
Acetovanillone	0.03±0.00	0.27±0.01	0.04±0.02	0.83±0.20	1.39±0.09	2.19±0.19	1.74±0.47	2.73
Guaiacylacetone	0.08±0.01	0.51±0.03	0.03±0.01		3.72±0.25	3.26±0.28	0.73±0.03	0.91
Coniferylaldehyde	N/A	N/A	0.14±0.09	2.70±0.70	11.73±0.80	5.41±0.47	4.84±1.14	5.75
				Syringol and substituted syringols				
Syringol	0.01±0.00	0.15±0.01	N/A	5.51±1.40	0.60±0.04			0.36
4-methylsyringol	N/A	N/A	N/A	2.91±0.73	N/A	N/A		0.86
4-ethylsyringol	0.02±0.00	0.12±0.01	N/A	3.82±0.97	2.37±0.16	0.10±0.01	N/A	N/A
4-Allylsyringol	N/A	N/A	N/A	0.99±0.25	N/A	N/A	N/A	N/A
4-propylsyringol	0.01±0.00	0.05±0.00	N/A	1.18±0.30	2.05±0.14	0.04±0.00	N/A	N/A
Syringaldehyde	0.23±0.05	0.46±0.02	0.02±0.01	1.76±0.45	23.10±1.57	1.73±0.15		0.78
Acetosyringone	0.26±0.03	0.81±0.04	N/A	1.46±0.23	6.16±0.42	0.42±0.04		0.65
Propylsyringone	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Butylsyringone	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
Sinapylaldehyde	0.13±0.03	<0.01	N/A		6.41±0.43	0.16±0.01		

[a]Wiregrass/ longleaf pine (Ocala National Forest, FL)

N/A compound not reported

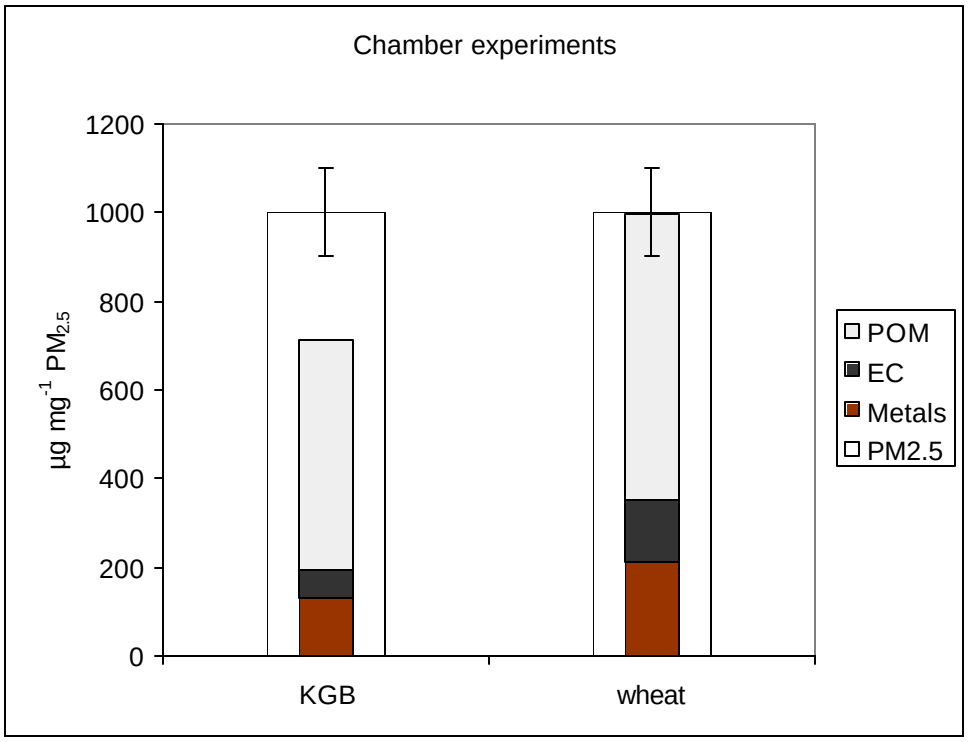

Figure 1. Major constituents found in $PM_{2.5}$ from smoke of wheat and KBG stubble burning in chamber experiments. Transparent bar illustrates the gravimetrically determined $PM_{2.5}$ mass, and POM mass was estimated using a scale factor of 1.4.

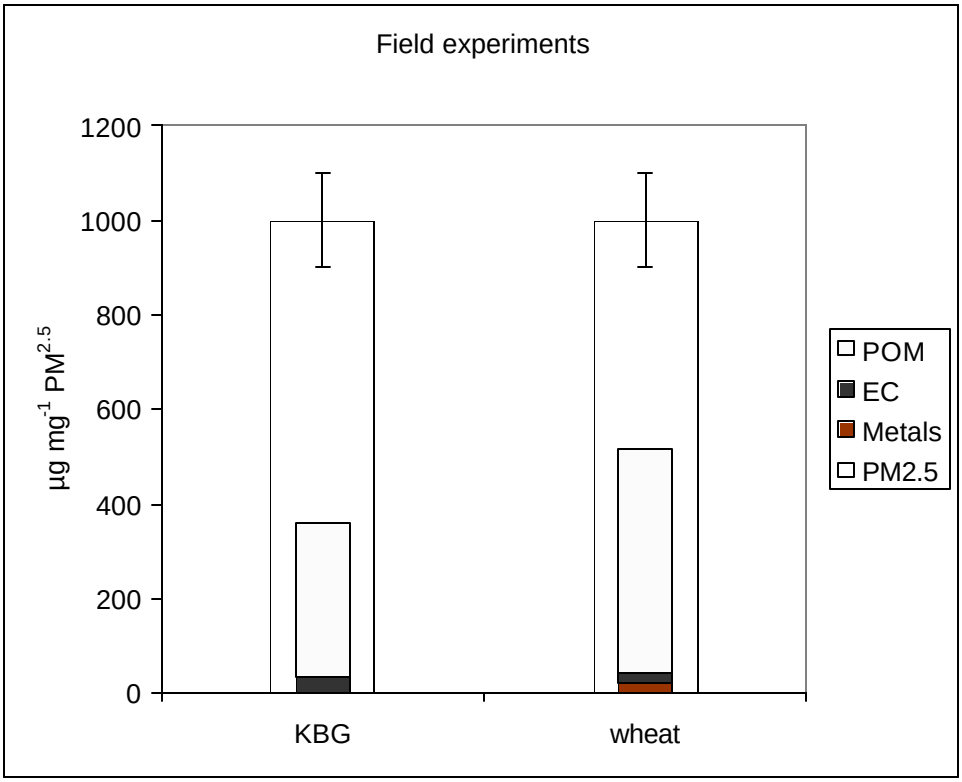

Figure 2. Major constituents found in $PM_{2.5}$ smoke from field burning of wheat and KBG stubble in the fall of 2004 and spring of 2005. KBG smoke samples were only collected in the fall of 2004, and no tracer elements were analyzed from these smoke PM samples. Transparent bar illustrates the gravimetrically determined $PM_{2.5}$ mass, and POM mass was estimated using a scale factor of 1.4.

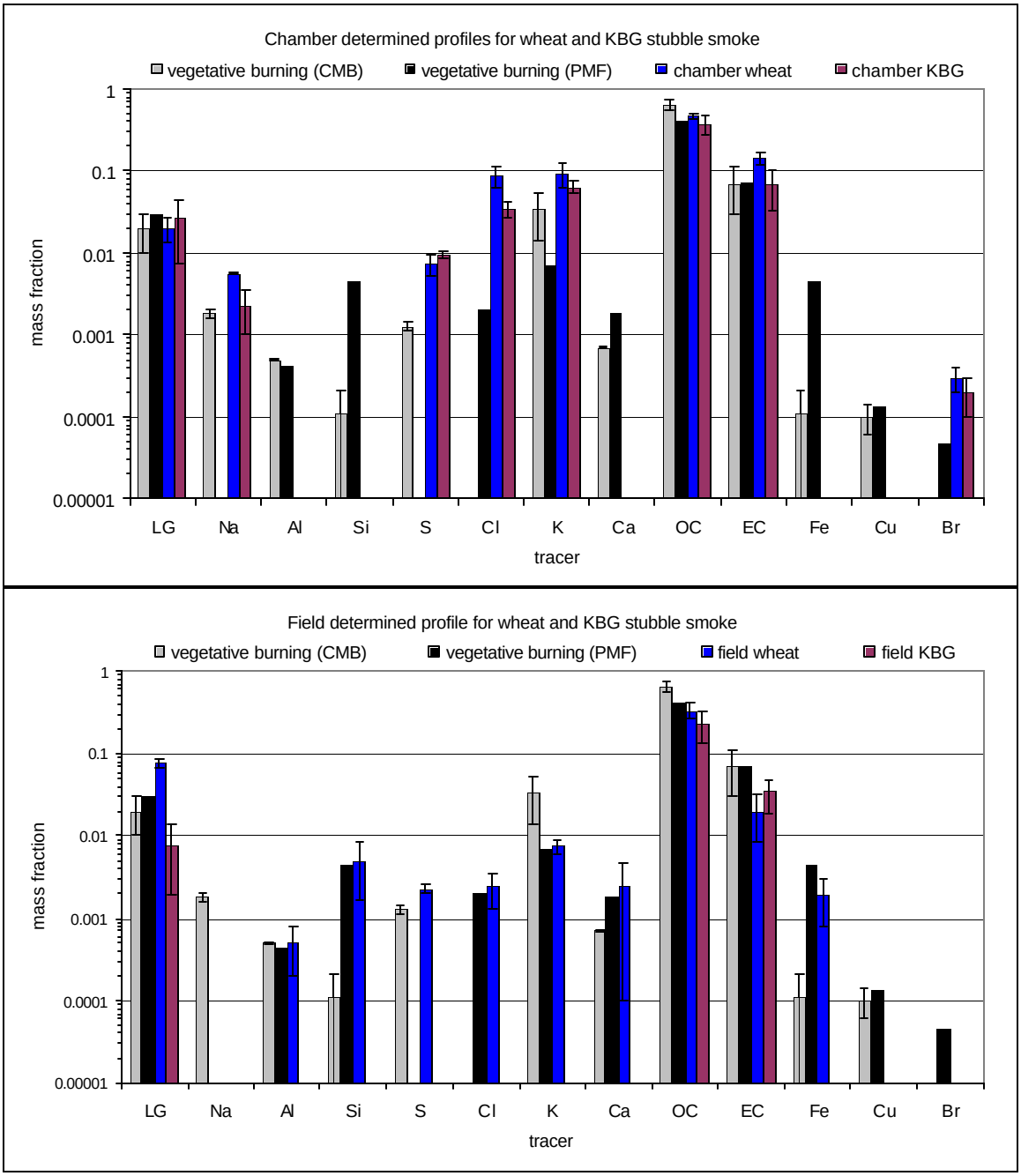

Figure 3. Comparison between the experimentally determined smoke profiles from wheat and KBG stubble burning with the vegetative burning profiles used in a source apportionment study in eastern Washington (Jimenez et al., 2006). This study used two models, which included a composite of vegetative burning profile (CMB model) and a statistically determined profile (PMF model) to resemble smoke from regional agricultural field burning.

Chapter 4

Filter Loading Corrections for Real-time Aethalometer Measurements of Fresh Diesel Soot

Filter Loading Corrections for Real-time Aethalometer Measurements of Fresh Diesel Soot

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ABSTRACT

In this study, a correction was developed for the aethalometer in order to measure real-time BC concentrations from fresh Diesel exhaust. The relationship between the actual mass-specific absorption coefficient for BC and the BC-dependent attenuation coefficients was determined from experiments conducted in a Diesel exposure chamber that provided constant concentrations (55±1 μg m^{-3}) of $PM_{2.5}$ (particulate matter less than 2.5 μm in aerodynamic diameter) from Diesel exhaust. The possible interference of adsorption of semi-volatile organic gases by the instrument's filter tape was investigated for fresh Diesel exhaust using paired aethalometers, one of which was operated with a diffusion denuder and the other without. On average, a 13% reduction in the $PM_{2.5}$ concentration was observed when using the activated carbon-impregnated foam denuder with Diesel generated PM. However, both un-denuded and denuded aethalometers reported concentrations decreasing with time for both infrared and UV absorbing PM when exposed to constant $PM_{2.5}$ concentrations from Diesel exhaust. This apparent decreasing rate in reported light absorbing PM concentration was used to derive a correction for the loading effect of strongly light absorbing particles (e.i. Diesel soot) on the aethalometer filter tape. The experimentally determined specific attenuation, s_{ATN} = 23.3±4.8 m^2 g^{-1} at ? =880 nm may be overestimated due to uncertainties in determining the split between organic carbon (OC), and elemental carbon (EC) from the thermal optical transmission method, which translated into an apparently large multiple scattering effect of the filter matrix for Diesel generated soot.

Keywords: Aethalometer, light absorption, Diesel soot, SVOC artifact, SVOC denuder, black carbon.

4.1 INTRODUCTION

Carbonaceous aerosols are composed mainly of organic carbon (OC), some of which are semi-volatiles, and elemental carbon (EC), a measure of black carbon aerosol (BC). Carbonaceous aerosols may have a detrimental impact on human health from both acute and chronic exposures, since they are a component of fine particulate matter and thus are able to penetrate into the lower respiratory system (Samet et al., 2000; Pope et al., 2002). Susceptible populations include those suffering chronic obstructive pulmonary disease (COPD), cardiovascular patients, and asthmatic children (Romieu et al., 1996; Peters et al., 1997; Yu et al., 2000; Ostro et al., 2001; Wargo et al., 2002). In addition, carbonaceous aerosol influences climate directly and indirectly through light extinction in the atmosphere (Adams et al., 1990; Horvath, 1993; Myhre et al., 2001) and can lead to low visibility (Crutzen and Andreae, 1990; Gebhart, et al., 2001).

It is known that the absorption efficiency of BC aerosol varies depending on the source and chemical composition (Liousse et al., 1993; Petzold and Niessner, 1995; Bond et al., 1999; Lavanchy et al., 1999; Schnaiter et al., 2003), and the assumption that all light absorbing material is due to the presence of BC aerosol is not always accurate (Gillespie and Lindberg, 1992; Malm and Kreidenweis, 1997; Caquineau et al., 1998; Arimoto et al., 2002; Kirchstetter et al. 2004).

Some organic carbon (OC) may have light scattering and absorption properties, as well. Semi-volatile organic compounds (SVOC) make up a fraction of the OC and they may partition between particulate and vapor phases in the atmosphere or during sampling depending upon temperature and molecular weight. A positive sampling artifact often results from adsorption of these compounds onto the filter media or collected particles

during sampling (Turpin et al., 1994; Eatough et al., 1995; Kirchstetter et al., 2001; Pang et al., 2002). These compounds may produce enhancements in light absorption, which in turn could affect the optical determination of BC aerosol concentrations.

Light absorption efficiencies of aerosols embedded in a reflective filter matrix are known to be enhanced compared to the same aerosols in the atmosphere (Sadler et al., 1981; Jennings et al., 1993; Bodhaine, 1995; Lavanchy et al., 1999; Arnott et al., 2005). For an early version of the aethalometer operating with an incandescent lamp, a value of $s_{ATN} = 19\ m^2\ g^{-1}$ was used to translate changes in light attenuation through a quartz filter into BC mass concentration (Hansen et al., 1984). This value was compared to the absorption efficiency of similar BC aerosol in the air ($s_{abs} \sim 10\ m^2\ g^{-1}$, Horvath, 1993) to account for absorption enhancements due to multiple scattering within the filter matrix (Jennings et al., 1993; Bodhaine, 1995).

Further, an optical effect due to the accumulation of particles in the filter has been reported for the aethalometer (La Rosa et al., 2002; Weingartner et al., 2003, Arnott et al., 2005; Kirchstetter and Novakov, 2006) and similar applications of the light transmission method (Petzold et al., 2005; Virkkula et al., 2005). As the filter becomes loaded with particles, the extent of enhancement of the light absorbed by the embedded BC decreases, which results in lower reported BC concentrations for loaded filters compared to lightly loaded filters. Weingartner et al. (2003) reported that this effect is more pronounced for freshly emitted soot than for aged atmospheric aerosol. The current aethalometer algorithm used to translate filter light attenuation into BC mass concentration does not correct for this loading effect.

Weingartner et al. (2003) also noted a marked increase in the enhancement of light absorbed by the BC when the Diesel soot was coated with transparent, secondary organic aerosol. This added enhancement was attributed to the condensation of organic vapors onto the aethalometer's filter. Therefore, they recommended the use of a denuder to remove vapor phase OC to minimize this enhancement effect, particularly when high concentrations of condensable gases are sampled.

In this study, we examine these artifacts using a constant source of Diesel soot. Using a constant particle emission source, we were able to separate the enhancement in the light absorption caused by multiple scattering in a relatively clean filter from those due to particle mass buildup and to develop a correction for both artifacts for fresh Diesel soot. We also investigated the effects of using a diffusion denuder when sampling fresh Diesel exhaust, as well as ambient $PM_{2.5}$ and environmental tobacco smoke (ETS).

4.2 METHODS

Two portable versions of the dual-wavelength aethalometers (AE41 and AE42, Magee Scientific Company, Berkeley, CA) were simultaneously exposed to a controlled concentration (55±1 μg m^{-3}) of ultra-fine Diesel generated particles (soot). A denuder was placed upstream of one of the collocated instruments to remove vapor-phase SVOC; the other was operated without a denuder.

4.2.1. Foam diffusion denuder

The diffusion denuder was made of activated carbon coated foam disks placed in a cassette body (25 mm diameter, Cole-Parmer Inc., part No. 10380-00), between sections of Tygon tubing. The impregnated foam was made of fine activated carbon particles (<10 μm diameter) incorporated into open-cell polyurethane plastic material during fabrication. Additional information regarding the performance of the activated carbon-coated foam as a denuder is reported elsewhere (Pang et al., 2002). The porosity and thickness of the foam used in this study was 100 ppi and 0.95 cm, respectively (Stephenson & Lawyer, Inc., Dalton, GA., part No. 80608).

We employed this denuder to investigate SVOC adsorption onto the quartz filter tape in the aethalometer and, thus, reduce the enhancement of light and the reported BC concentrations. When using the denuder, it was important to distinguish between the intended removal of SVOC and the unintended removal of particles because particle removal by the denuder would also have an effect on a filter-based optical method to estimate BC aerosol concentrations. Prior to the Diesel chamber experiments with the aethalometers, the performance of the activated carbon coated foam denuder, specifically with respect to $PM_{2.5}$ mass, OC and EC mass, was examined for ambient $PM_{2.5}$ and fresh Diesel soot. Ambient $PM_{2.5}$ was collected from collocated pairs of 12-hr integrated $PM_{2.5}$ samples (one with the denuder) operated from 08:00 am to 08:00 pm and from 08:00 pm to 08:00 am, PST. These samples were collected with single-stage, 10 L min^{-1} Harvard Impactors ($HI_{2.5}$) (Air Diagnostics Inc., Naples, ME). One $HI_{2.5}$ pair sampled $PM_{2.5}$ onto 37-mm Teflon filters, and another pair onto quartz filters. The ambient $PM_{2.5}$ samples were collected in the fall of 2002 from an ambient monitoring site located in Pullman,

WA (see Jimenez et al., 2006 for more details regarding the monitoring site). Field blanks and duplicates were deployed so that they comprised at least 10% of the total $HI_{2.5}$ sample size. The precision (1.2 µg m^{-3}) and accuracy (3%) of the $HI_{2.5}$ have been reported elsewhere (Liu et al., 2002).

The foam denuder was also tested with environmental tobacco smoke (ETS) at a chamber facility located at Lawrence Berkeley National Laboratory (LBNL), Berkeley, CA., in an experiment designed to determine if the foam material produces changes in the particle size distribution of the sampled aerosols. For this experiment, a 10-stage piezoelectric quartz crystal microbalance (QCM) cascade impactor (Model PC-2, 240 mL min^{-1}, with impactor stages for 0.05, 0.1, 0.2, 0.4, 0.8, 1.6, 3.2 and 6.4 µm particles, California Measurements Inc., Sierra Madre, CA) was used to measure and compare particle size mass distributions of ETS upstream and downstream of the diffusion denuder. The foam denuder particle size cut point (d_c), defined as the particle size with 50% penetration, was determined from an empirical model developed by Vincent et al. (1993), which estimates d_c through a porous foam as function of thickness, porosity (density) and face velocity (ratio of the volumetric flow rate to cross section area perpendicular to the flow) through the media. The use of foam as a size selective inlet has been extensively reported elsewhere (Vincent et al., 1993; Chen et al., 1998; Kenny et al., 1998; Kenny et al., 1999).

4.2.2. Diesel chamber

The Diesel chamber was housed in the Department of Environmental and Occupational Health Sciences at the University of Washington. The chamber dimensions

are 8.8 x 5.5 x 2.4 m with a total volume of 116 m^3. The volumetric flow rate through the chamber was 28.3 m^3 min^{-1} and the incoming air was filtered so that the PM concentration inside the chamber was free of background contamination. Diesel soot was generated from a turbocharged direct-injection 5.9-liter Cummins B-series Diesel engine (6BT5.9G6, Cummins, Inc., Columbus, IN), which is comparable to engines used in delivery trucks and school buses. The engine drove a 100 kW generator connected to an electric load bank (Simplex, Springfield, IL), which was set at 75 kW. The engine fuel was highway grade Diesel No 2 un-dyed, which is commonly used in delivery vehicles.

The $PM_{2.5}$ concentration inside the chamber was controlled by diverting Diesel exhaust from the engine into the air flowing through the chamber. A variable speed fan controlled by a system that uses two light scattering nephelometers (one sensing downstream of the chamber and the other inside the chamber) provided feedback to the system to adjust the amount of diverted Diesel exhaust, in order to achieve and maintain a target $PM_{2.5}$ concentration. Under conditions of constant Diesel exhaust $PM_{2.5}$ concentration, the chamber exhibited a linear relationship between elemental carbon (EC) and $PM_{2.5}$ mass concentration (intercept= -6.1, slope= 0.85, R^2= 0.97).

4.2.3. Measurements

Each experiment was designed to avoid systematic errors from instrument calibration issues and/or from repeatedly using the same monitor with the denuder. The experiments are summarized as follows: (a) initial collocation with no denuder upstream and, when required, a correction factor was applied to compare data from both instruments; (b) one instrument with denuder and the other instrument without it; and (c)

denuder switched between the aethalometers. Additionally, we audited and calibrated the flows of the instruments onsite using a flow meter (Dry Cal, BIOS International Corporation, Butler, NJ).

In order to verify constant conditions and to compare chamber generated Diesel soot to ambient measurements and other experiments reported in the literature, several additional chamber measurements were performed. These included continuous $PM_{2.5}$ concentrations from a Tapered Element Oscillating Microbalance (TEOM) monitor with a $PM_{2.5}$ inlet (1-min. Series 1400a, Thermo Electron Co.); light scattering coefficient, b_{scat}, from a nephelometer (1-min, M903, Radiance Research, Seattle, WA). The nephelometer was calibrated using zero air and carbon dioxide (CO_2) for span setting. In addition, integrated $PM_{2.5}$ samples were taken from collocated single-stage 5 L min^{-1} low-volume samplers (low-vol) (Airmetrics Inc., Eugene, OR). Two-stage filter cassettes (47-mm) with Teflon filter (2 µm pores part No 7592-104, Whatman Inc., Clifton, NJ) and quartz filter after Teflon, as well as single-stage filter cassettes with quartz (part No 1851047, Whatman Inc., Clifton, NJ) were used with the samplers to estimate OC fractions, SVOC artifact, and EC. Additionally, for the experiment conducted at relatively constant concentrations of $PM_{2.5}$ from Diesel exhaust, two EcoChem samplers (EcoChem Analytics, League City, TX) were deployed to measure particle active surface area (PASA) and total particle-bound polycyclic aromatic hydrocarbons (PPAHs). These instruments have been used to characterize aerosols based on the relationship between particle active surface area and the concentration of particle-bound PAHs (Velasco et al., 2004; Ott and Siegmann, 2006).

4.2.4. Sample and data analysis

$PM_{2.5}$ collected on the Teflon filters was analyzed gravimetrically using a microbalance (model UMT2, Mettler-Toledo, Inc., Columbus, OH). The filters were conditioned at a constant temperature (22.2±1.8 °C) and relative humidity (34.8±2.5 %) for at least 24 hours prior to weighing. Sections of the quartz filters (1.5 cm^2) were analyzed for OC and EC via thermal optical evolved gas analysis (Thermal Optical Transmittance, TOT, Sunset Laboratory Inc., Tigard, OR) using a modified version of the NIOSH 5040 method (Pang et al., 2002). The TOT carbon analyzer was calibrated using a standard solution of sucrose (20 µL of 4.5 g C L^{-1} solution = 90 µg C). More details about the temperature steps, carrier gases and standards used in this thermal optical analysis are reported in Pang et al. (2002).

A correction for the positive OC sampling artifact was applied by subtracting the back (after Teflon) quartz filter OC concentration from the corresponding concentration obtained from the collocated single quartz filter (Fitz, 1990; Turpin et al., 1994). Black carbon concentrations from the aethalometer were compared to the EC concentrations measured by thermal optical analysis of the quartz filters. Data collected with both aethalometers were compared to determine differences in the measurements when using the denuder on the aethalometer. In addition, aethalometer measurements were compared to other PM measurements, including $PM_{2.5}$ concentration, b_{scat}, PASA and PPAHs. This was done to evaluate the temporal behavior of the aethalometer measurements during the chamber experiment at constant PM concentrations. Finally, a correction was proposed for the aethalometer to account for loading effect and light absorption enhancements due to multiple scattering of the filter matrix. The latter correction was developed from

scaling the aethalometer b_{ATN} measurements to the EC information obtained from the TOT analysis.

4.2.5. Model framework

The primary goal of this study was to develop a correction factor for the aethalometer algorithm that could account for both absorption enhancements due to multiple scattering of the filter matrix and for the loading effect. This factor would be specific for air containing fresh Diesel exhaust dominated aerosols.

The optical attenuation (*ATN*) of light by particles deposited in the quartz filter is given by the following relationship;

$$ATN = -100 \times \ln\left(I / I_0 \right) \qquad (1)$$

Where, I_0 is the intensity of the incoming light and I is the light intensity remaining after passing through the filter media and collected particles. Aethalometers measure light attenuation through a highly light scattering quartz filter fiber matrix. The light scattered away from the detector by particles collected on the filter is assumed negligible compared to the filter matrix light scattering (Hansen et al., 1984). The attenuation coefficient, b_{ATN}, has units of m^{-1} and is given by:

$$b_{ATN} = \frac{A}{Q}\frac{\Delta ATN}{\Delta t} \qquad (2)$$

where A is the filter collection area (m^2), or "spot", Q is the volumetric flow rate (m^3 min^{-1}) and ? ATN is the change in light attenuation during the time interval, ? t (min). The mass concentration of BC aerosol, M_{BC}, (g m^{-3}) is then calculated from the attenuation coefficient,

$$M_{BC} = \frac{b_{ATN}}{s_{ATN}} \qquad (3)$$

where s_{ATN} is the attenuation efficiency of BC in the filter substrate, with a manufacturer's recommended value of s_{ATN} = 16.6 m^2 g^{-1} at ?= 880 nm, and 39.5 m^2 g^{-1} at ?= 370 nm for the dual wavelength aethalometer, based on the relationship between attenuation and BC concentration determined by thermal optical analysis (Gundel et al., 1984).

The light absorption from the particles can be related to the total light attenuation (filter plus particles) by accounting for multiple scattering and particle loading effects on the filter matrix. Weingartner et al. (2003), suggests a relationship between particle absorption coefficient, b_{abs}, and the attenuation coefficient, b_{ATN}, for the aethalometer by introducing two correction factors. The first correction factor, *C*, accounts for absorption enhancements due to multiple scattering including enhanced absorption resulting from quartz filter adsorption artifact, and the other correction factor, *K(ATN)*, accounts for a non-linear absorption response to filter loading, as follows;

$$b_{abs} = \frac{b_{ATN}}{C \cdot K(ATN)} \qquad (4)$$

In this study, we experimentally determined these two correction factors [*C* and *K*(*ATN*)] for Diesel soot based on 1-min averaged aethalometer measurements collected during a 2-hr period of constant concentrations of Diesel exhaust particle mass. The correction to account for a non-linear absorption response to filter loading, *K(ATN)*, was defined as,

$$K(ATN) = a + b \times \exp(-ATN/100) \qquad (5)$$

where *a* and *b* are regression coefficients determined from the expressions represented in Equation (6) versus Equation (5), and *K*(*ATN*) was derived from the relative difference between the increments of attenuation between two consecutive measurements. The relative increment in attenuation in a ?t interval is determined from aethalometer measurements as follows;

$$K(ATN) = \frac{\Delta ATN(t)}{\Delta ATN(0)} \qquad (6)$$

where ? *ATN*(t) is the difference between two consecutive measurements [e.i. $ATN(t+1) - ATN(t)$], and ? *ATN*(0) is the difference between the first and second reported measurements for light attenuation at the beginning of the measuring cycle of the instrument (new filter spot).

The multiple scattering effect due to the filter matrix, *C*, was derived by comparing the experimentally determined attenuation efficiency, s_{ATN}, to the mass specific absorption efficiency, $s_{abs.}$ The s_{abs} was determined from the difference between the extinction efficiency, s_{ext}, and the scattering efficiency, s_{scat}, of Diesel soot in air. The s_{ATN} for Diesel soot was determined by means of the aethalometer, at a constant exposure to Diesel-generated PM and corrected for the loading effect. The s_{scat} was determined on-site by means of nephelometer, and the s_{ext} values of Diesel soot in air were extracted from Schnaiter et al. (2003), who conducted experiments with a flow tube spectrometer.

4.3 RESULTS AND DISCUSSION

4.3.1. The foam denuder

The configurations of the foam thickness and the face velocity were intended to achieve d_c larger than 2.5 µm to avoid removing particles in the intermodal range (dp~0.1-2.5 µm). The predicted d_c, for the different configurations of the foam denuder ranged between 3 to 5 µm. Table 1 summarizes the $PM_{2.5}$ concentrations and carbonaceous fractions for the 45 $PM_{2.5}$ paired samples (with and without the diffusion denuder) collected at the outdoor site in Pullman. When the denuder was used with the $HI_{2.5}$ sampler, on average a 15% reduction in the $PM_{2.5}$ concentration was observed. Furthermore, a higher reduction (28%) of OC and almost no reduction (2%) in the EC fraction were observed on the denuded samples. The diffusion denuder used with the $HI_{2.5}$ resulted in lower $PM_{2.5}$ concentrations for ambient aerosols with an average ratio of $OC/PM_{2.5} = 0.29 \pm 0.20$, and had the greatest effect on the most volatile fraction (OC1) of the organic carbon. Similarly, when sampling Diesel exhaust in the chamber experiment, a greater reduction in the OC fraction of $PM_{2.5}$ (~80%) was observed for denuded samples, mainly in the most volatile fractions of OC. For the outdoor samples, the EC was not significantly different ($p = 1.67$, N= 46) for the samples collected with and without a denuder, while the more volatile fractions of OC showed significant differences ($p<0.01$, N= 46). These experiments suggest that the denuder removes material that would otherwise be counted as $PM_{2.5}$ mass. However, the observed ambient EC concentrations were considerably lower (~0.5 µg m^{-3}) compared to those observed in the chamber experiments with Diesel exhaust (~35 µg m^{-3}). In the latter experiment a greater

reduction in EC was observed from using the denuder with the integrated samplers. These results are discussed in more details in succeeding sections.

To further ensure that the denuder does not significantly change the size distribution in the $PM_{2.5}$ range, the particle size distribution before and after the denuder was examined for ETS (temperature 21±1 ^{o}C, RH= 52±2%, $PM_{2.5}$~ 50 µg m^{-3}). The data showed that the foam denuder did not cause significant changes to the particle mass size distribution (p>0.05, N= 9).

4.3.2. Diesel chamber experiments

TEOM $PM_{2.5}$, nephelometer scattering coefficient (b_{scat}), particle active surface area (PASA), and total particle-bound PAHs (PPAHs) concentrations in the Diesel chamber experiment at constant $PM_{2.5}$ concentrations are shown in Figure 1. The time period of constant $PM_{2.5}$ concentrations between 14:00 and 16:00 hr (2-hr) was selected to test the aethalometer response to constant BC mass concentrations and to determine a correction factor, $K(ATN)$, to account for loading effect. Table 2 provides summary statistics for the PM parameters measured during the 2-hr run at a constant $PM_{2.5}$ concentration. Note that all parameters were rather constant (~3% variation) and highly correlated (r>0.87) to each other (Table 3). We found for this experiment that the ratio of PPAHs/PASA was 1.8±0.1 ng mm^{-2}, and was higher than similar ratios reported by Velasco et al. (2004) from measurements on a road near a working dump truck (~1.2 ng mm^{-2}) and averaged measurements (~1.0 ng mm^{-2}) reported from chasing a tractor-trailer truck on a California road (Ott and Segmann, 2006). This suggests that for this

experiment, the generated Diesel soot had more PAHs (SVOC) attached to the particle surface in proportion to the available surface area.

The un-denuded aethalometer measurements obtained during the same Diesel chamber experiment are shown in Figure 2. This figure includes uncorrected measurements for both channels (BC at 880 nm and UVPM at 370 nm) along with the observed $PM_{2.5}$ concentration. Note the recurring decrease in the aethalometer measurements of BC and UVPM concentrations (ratio UVPM/BC ~ 0.75) at constant $PM_{2.5}$ concentrations from diluted Diesel exhaust. This periodic behavior was observed in all measurement cycles (4 spots) and in both collocated aethalometers (sampling at 2.2 L min^{-1}) both with and without the use of the denuder. The reported *ATN* values increased continuously up to ~55 at 880 nm and 95 at 370 nm, which correspond to ~3.4 µg of diesel soot deposited in the filter spot as estimated from the $TEOM_{2.5}$ measurements. After the filter tape advanced to a clean spot, the first reported values of *ATN* were ~4 for BC and 7 for UVPM channels. Additionally, note from Figure 2 an apparent UVPM < BC signal (ratio UVPM/BC ~ 0.75) in the reported measurements. Ideally, the BC concentration (determined from absorption at 880 nm) should be about equal to the UVPM concentration (determined at 370 nm). However, the difference in the reported concentration of light absorbing PM from the two available channels is due to the preset attenuation efficiency determined from ambient aerosols as part of the manufacturer calibration, which does not necessarily represent the wavelength dependency of the attenuation efficiency of the Diesel soot generated in this experiment.

Table 4 summarizes results obtained using the diffusion denuder and applying an artifact correction based on an independent measurement of particle OC concentration

(quartz filter after Teflon). The percentage reduction in OC observed when using the denuder was consistent with that observed when applying the artifact correction to the front quartz filter. In both experiments the greatest reduction in OC mass occurred at the higher volatility (OC1-OC3) fractions of OC. The denuded sample did show a greater reduction in EC (15%) compared to similar reduction (2%) observed for the ambient $PM_{2.5}$ samples and, more relevantly, a 0% reduction for diesel chamber experiment #1.

When using the denuder, a reduction (~13 %) in both aethalometer channels was observed. Based upon the similar reduction observed in the EC concentration from collocated sampler (with denuder), this reduction in the aethalometer signal may be due to a combination of SVOC removal and some degree of BC particles scrubbing from the foam denuder used with the aethalometer.

The aethalometer values for BC at 880 nm and UVPM at 370 nm (from the manufacturer's algorithm) were compared to the EC concentration (determined from TOT analysis) during the 2-hr period at a constant $PM_{2.5}$ concentration. The average BC and UVPM concentrations at 880 and 370 nm (39.2±5.1 and 29.5±4.3 μg m^{-3} for undenuded and 33.7±4.7 μg m^{-3} and 26.4±4.2 μg m^{-3} for denuded aethalometer, respectively) were relatively similar to the EC concentration determined from thermal-optical analysis (35.1±6.1 μg m^{-3}). However, the decreasing trend in the temporal evolution of the aethalometer measurements (48.1? 31.5 μg m^{-3}; see Figure 2) at constant $PM_{2.5}$ concentrations, independent of the use of a denuder, suggest that the instrument overestimates BC concentrations when the filter spot is relatively unloaded and that it underestimates BC concentrations when the filter is loaded with Diesel soot.

4.3.3. Aethalometer correction

Linear regression applied to the data from Equation (6) versus Equation (5) (see Figure 3) was used to determine the coefficients a= 0.13 and b= 0.88 (R^2= 0.92) at 880 nm, in equation 5. Values for $K(ATN)$ were determined using the relationship presented in equation (6) applied to aethalometer measurements (N= 170) at constant concentrations of Diesel-generated PM (see Table 2). Nearly identical values were reported by Kirchstetter et al. (2006), who applied a similarly strong light absorbing BC (i.e., with a single scattering albedo of ~ 0.25) from a diffusion flame to develop a correction for real-time aethalometer data. The agreement between the two approaches suggests that the coefficients reported here can be used when using the aethalometer to sample aerosol characterized by low single scattering albedo in addition to Diesel soot.

A similar approach was used for correcting the attenuation measurements at 370 nm (UVPM), which gave the coefficients a= 0.38 and b= 0.67 (R^2= 0.95). The corrected b_{ATN} using the $K(ATN)$ correction for filter loading are shown in Figure 4 [corrected value = $b_{ATN} / K(ATN)$]. There is good agreement between the temporal evolution of the $PM_{2.5}$ concentration and the corrected b_{ATN} measured with the aethalometer. In addition, after applying the above correction, the Spearman's correlation coefficient, r (Table 4) improved (>4 percentage points) for all measured PM parameters.

After adjusting b_{ATN} for the filter mass loading effect (see Figure 4) the BC aerosol concentration was calculated using equation (3) and the manufacturer's recommended attenuation efficiency, (s_{ATN} = 16.6 m^2 g^{-1} at 880 nm, and 39.5 m^2 g^{-1} at 370 nm) and compared to 2-hr average values for EC taken from the TOT analyses. For the averaged b_{ATN} (b_{ATN} = 820±30 Mm^{-1} at 880 nm, and 1500±80 Mm^{-1} at 370 nm)

observed in the experiment (un-denuded aethalometer), the aethalometer BC concentrations determined at 880 and 370 nm overstated the TOT EC by ~50% and ~10%, respectively.

In order to quantify the multiple scattering effect of the aethalometer's filter matrix, the experimentally determined attenuation efficiencies (using equation 3, corrected b_{ATN}, and EC concentrations from the TOT analysis) (s_{ATN} = 23.3±4.8 m^2 g^{-1} at 880 nm, and 42.9±1.0 m^2 g^{-1} at 370 nm) were compared to the absorption efficiencies of Diesel soot measured in air. The extinction efficiency of Diesel soot (s_{ext}= 5.1 m^2 g^{-1} at 880 nm, and 14 m^2 g^{-1} at 370 nm) was estimated from Schnaiter et al. (2003), and scattering efficiency of Diesel soot (s_{scat}= 0.6 m^2 g^{-1} at 880 nm, and 3.0 m^2 g^{-1} at 370 nm) was determined from onsite nephelometer measurements (at 530 nm and extrapolated using wavelength dependence, $?^{-a}$ with a =1.9). The absorption efficiency, $s_{abs,}$ was obtained by subtracting s_{scat} from s_{ext}, and the values of C were determined by dividing the experimentally determined s_{ATN} by the calculated s_{abs}. Figure 5 shows the C values for fresh Diesel soot determined in this experiment and similar values reported by Weingartner et al. (2003) for similar aerosols. Note that these experimentally determined C values were higher than those previously reported for this instrument. This could be due to underestimation of EC from the TOT method (Thermal Optical Transmission) and NIOSH protocol used to determine the split between OC and EC, since the estimation of the C (multiple scattering enhancements) directly depends on the determination of the EC (Equation 3). In addition, studies show that when a particulate matter sample is analyzed with different thermal optical methods, the BC estimates vary considerably (Countess, 1990; Shah and Rau, 1991; Schmid et al., 2001, Watson et al., 2005).

The absorption coefficients, b_{abs}= 160±50 Mm^{-1} at 880 nm and 390±100 Mm^{-1} at 370 nm were determined for the chamber experiment at constant PM concentrations by using equation (4), with the aethalometer attenuation measurements corrected for loading and multiple scattering effects. As shown in Figure 6, the resulting aethalometer BC concentrations estimated from this proposed correction are in good agreement with the temporal behavior and magnitude of the concentrations of $PM_{2.5}$ and the averaged EC concentration determined from TOT analysis.

Finally, as a way of verification of derived *C* values, the average absorption coefficients, $b_{abs,}$ determined by the aethalometer at 370 and 880 nm were compared in Figure 7 with the expected wavelength dependent trend in light absorption by Diesel soot, which can be represented by the Ångström power law, $b_{abs} \sim ?^{a}$ with a= 1.1, as discussed in Schnaiter et al. (2003). This figure shows a consistent wavelength dependency for the b_{abs}, experimentally determined by means of aethalometer, in an environment dominated with Diesel soot and reported values for similar types of aerosols.

4.4. SUMMARY AND CONCLUSIONS

We have developed a correction for the aethalometer measurement that enables reliable measurement of real-time high concentrations of BC from Diesel exhaust. This included a correction for absorption enhancements due to multiple scattering of the filter matrix, and a non-linear response of the instrument as the filter becomes loaded with light absorbing particles. We used a specially designed chamber for developing this correction due to its capabilities to actively maintain constant concentrations of $PM_{2.5}$ from Diesel

exhaust inside the chamber. This was necessary to determine the optical artifact occurring as the filter loads with particles.

Additionally, we examined the effects of semi-volatile organic compounds on the optical absorption of black carbon by equipping an aethalometer with a diffusion denuder designed to remove SVOC interferences. When using the activated carbon-impregnated foam denuder on the aethalometer, an average reduction of 13 % was observed at both wavelengths. Thermal optical evolved gas analysis from collocated samples demonstrated that this reduction was mainly due to the most volatile fraction of organic carbon, but also some of the EC particles. Further work should include testing the proposed correction with mixed aerosol, including non-absorbing aerosols, as well as in ambient air with diesel exhaust and environmental tobacco smoke. In addition, future work should include additional instrumentation and calibration methods to determine EC/BC mass concentrations.

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(*Tables and Figures follow references*)

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Table 1

Summary of basic statistics for $PM_{2.5}$ data (μg m^{-3}) without (w/o) and with denuder (denuder) collected in 2002 at outdoor site in Pullman, WA.

Parameter	$PM_{2.5}$		TC		OC		EC	
	w/o	denuder	w/o	denuder	w/o	denuder	w/o	denuder
Mean	12.5	10.5	4.2	3.1	3.6	2.6	0.55	0.54
Standard Deviation	6.0	5.4	2.1	1.8	1.8	1.5	0.58	0.46
25 percentile	9.1	7.4	2.9	1.8	2.5	1.6	0.05	0.22
Median	11.5	10.3	4.1	3.1	3.6	2.5	0.47	0.51
75 percentile	15.5	13.6	5.7	4.3	4.7	3.6	0.69	0.74
Observations (N)	45	45	46	46	46	46	46	46

12-hr averaged integration time

Table 2

Summary of basic statistics for continuous PM parameters measured at Diesel chamber experiment Seattle, WA during two-hours of constant $PM_{2.5}$ concentrations.

Parameter	TEOM $PM_{2.5}$ (μg m^{-3})	[1]b_{scat} (Mm^{-1})	[2]PASA (mm^2 m^{-3})	[3]PPAHs (ng m^{-3})
Mean	54.6	95	470	856
Standard Deviation	1.0	3	11	23
25 percentile	54.1	92	460	834
Median	54.6	94	470	852
75 percentile	55.4	96	478	865
Observations (N)	121	121	121	121

Integration time 1-min averaged

[1]Sacttering coefficient at 530 nm

[2]Particle active surface area

[3]Particle-bound total polycyclic aromatic hydrocarbon

Table 3

Summary of Spearman's correlation coefficients (N=200) between $TEOM_{2.5}$, b_{scat}, PASA and PPAHs observed during the Diesel chamber experiment.

	$TEOM_{2.5}$	Neph b_{scat}	PASA	PPAHs	b_{ATN}/K 880 nm	b_{ATN}/K 370 nm
$TEOM_{2.5}$	1				0.94	0.91
Neph b_{scat}	0.94	1			0.97	0.97
PASA	0.98	0.96	1		0.96	0.94
PPAHs	0.98	0.97	0.99	1	0.97	0.95
b_{ATN} 880 nm	0.87	0.93	0.90	0.91	-	
b_{ATN} 370 nm	0.84	0.92	0.87	0.89		-

Table 4

Comparison between SVOC artifact correction from using quartz after Teflon and from using the foam denuder during $PM_{2.5}$ sampling of Diesel generated particles.

	Diesel chamber experiment #1				Diesel chamber experiment #2		
Parameter ($\mu g\ m^{-3}$)	Front quartz filter	Quartz filter after Teflon	Artifact corrected	Reduction %	Front quartz filter	Upstream foam	Reduction %
EC	35.1±6.1	0.0±1.2	35.1±6.2	0	24.4±3.3	20.7±3.1	15
OC	39.2±5.3	27.3±4.8	11.9±7.1	70	44.0±4.3	11.6±2.6	73
OC1	13.3±3.2	10.9±3.8	2.4±5.0	82	18.4±3.7	0.7±0.1	96
OC2	12.4±3.1	11.4±2.9	1.0±4.2	95	14.3±2.9	3.2±0.6	78
OC3	4.2±1.7	3.5±1.6	0.7±2.3	82	4.9±1.0	2.0±0.4	59
OC4	8.9±2.5	1.1±0.2	7.8±2.5	12	6.1±1.2	5.3±1.1	13
Pyro C	0.3±0.2	0.4±0.1	-	-	0.4±0.1	0.5±0.1	-

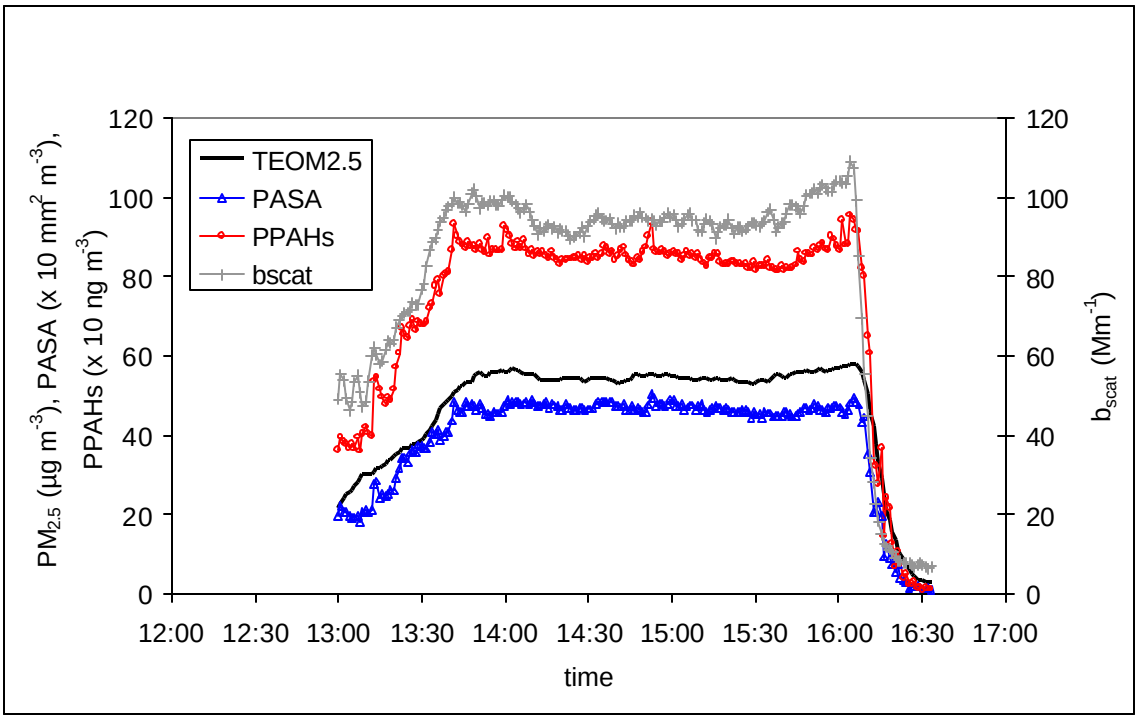

Figure 1. Temporal distribution of $PM_{2.5}$ concentration, particle active surface area (PASA), total particle-bound polyaromatics (PPAHs), absorption coefficient (b_{abs}) and scattering coefficient (b_{scat}) during exposure to Diesel soot. Note constant levels of $PM_{2.5}$ between 14:00 and 16:00 hr.

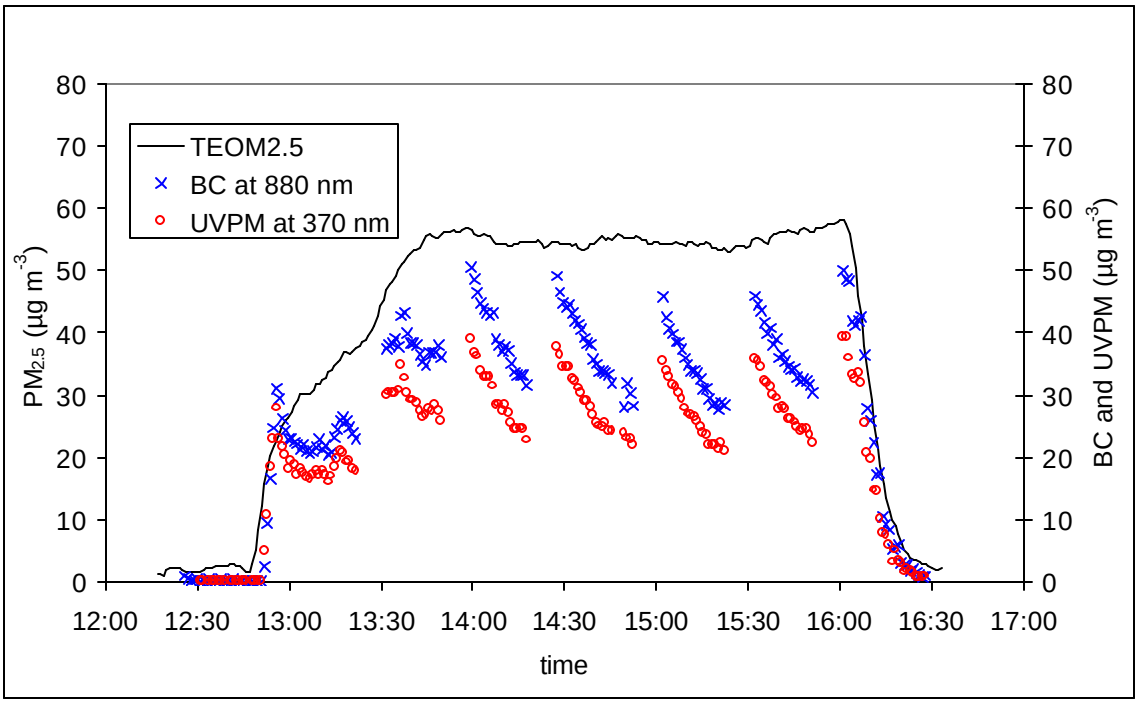

Figure 2. Temporal distribution of $PM_{2.5}$ concentration and BC and UVPM aethalometer measurements during diesel soot exposure. Note that at constant levels of $PM_{2.5}$ the aethalometer measures a decaying trend in the BC and UVPM concentration.

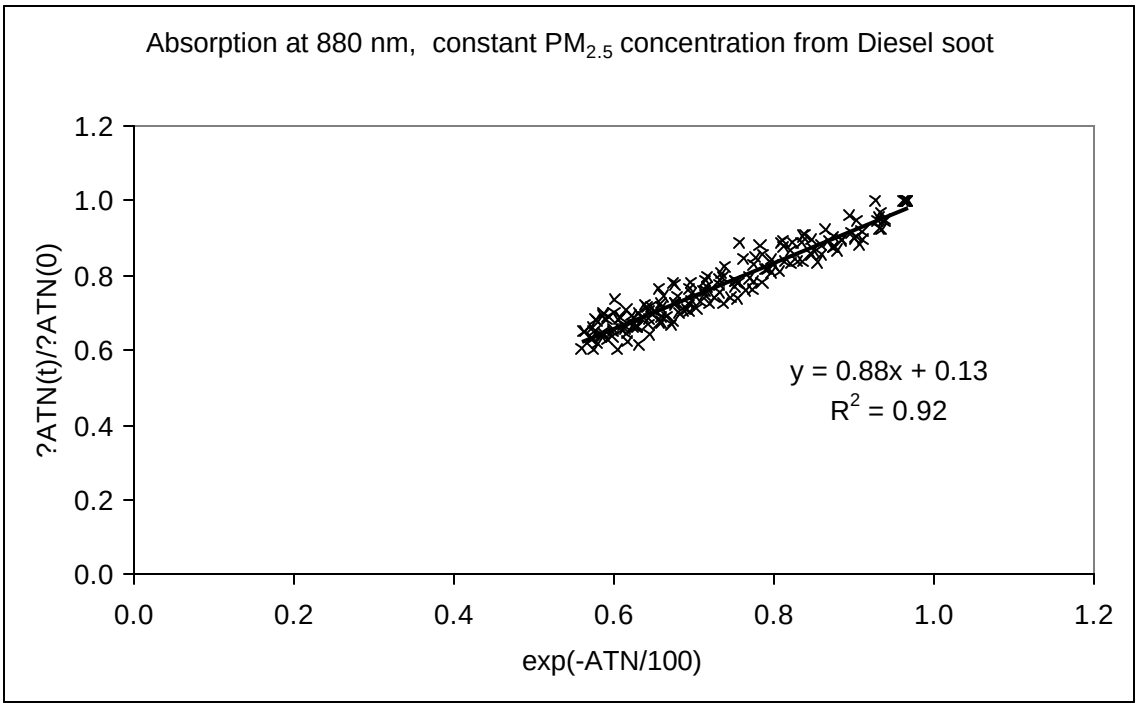

Figure 3. Linear regression applied to determine the regression coefficients *a* and *b* at 880 nm used to correct for particle loading effect in the aethalometer measurements.

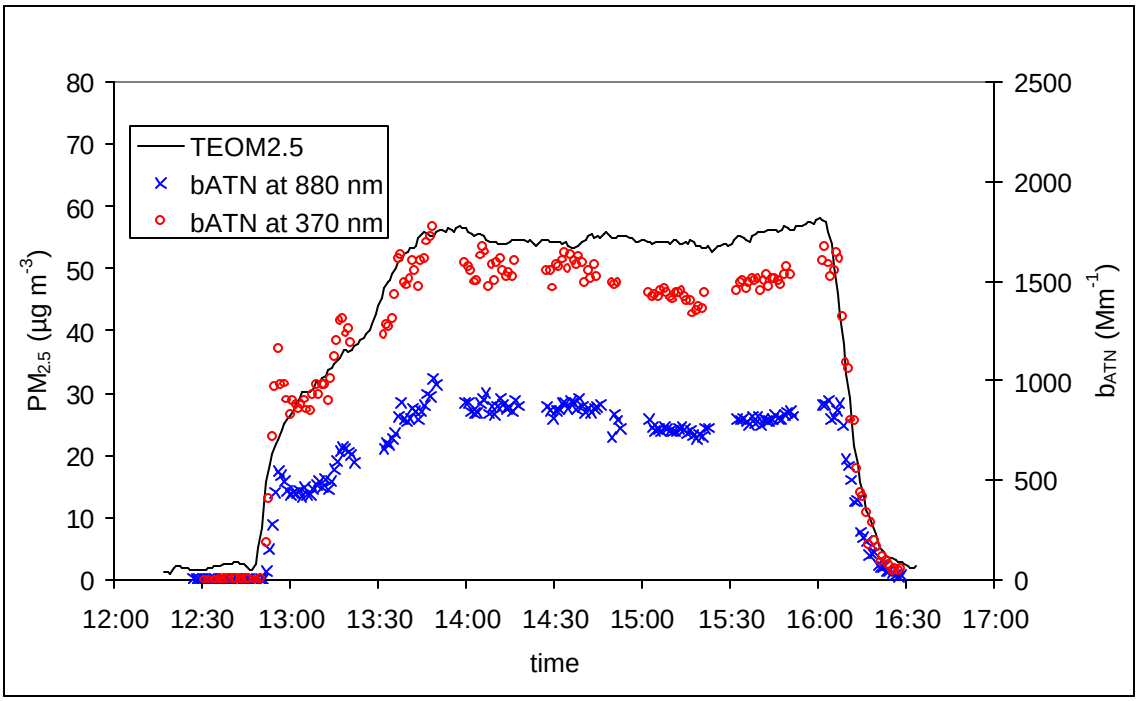

Figure 4. Correction for particle loading effect K(ATN) applied to the attenuation coefficient determined with the aethalometer. Note that the b_{ATN} measured at both wavelengths matches the temporal behavior of the $PM_{2.5}$ concentration.

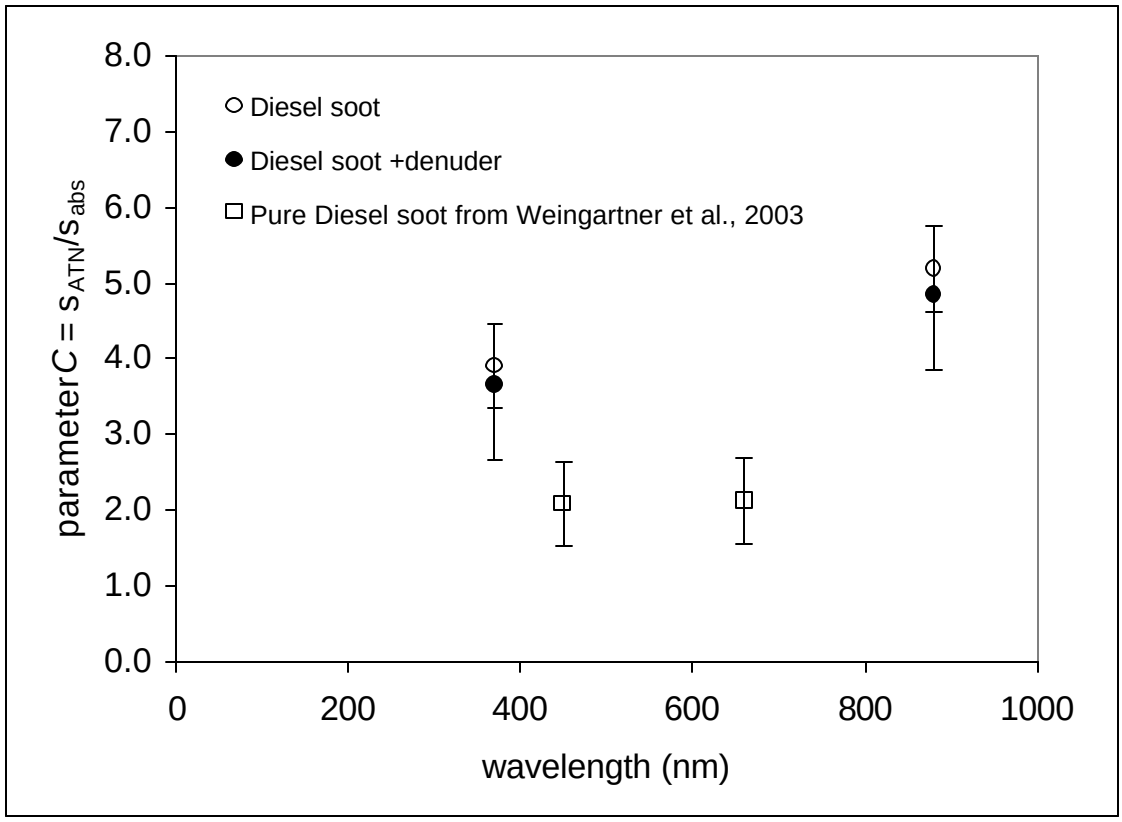

Figure 5. Comparison between the experimentally determined values for multiple scattering effects, C of the aethalometer filter (circles) and similar values reported by Weingartner et al. (2003) from aethalometer experiments (open squares). C was calculated as s_{ATN} (calculated from this work)/ s_{abs}.

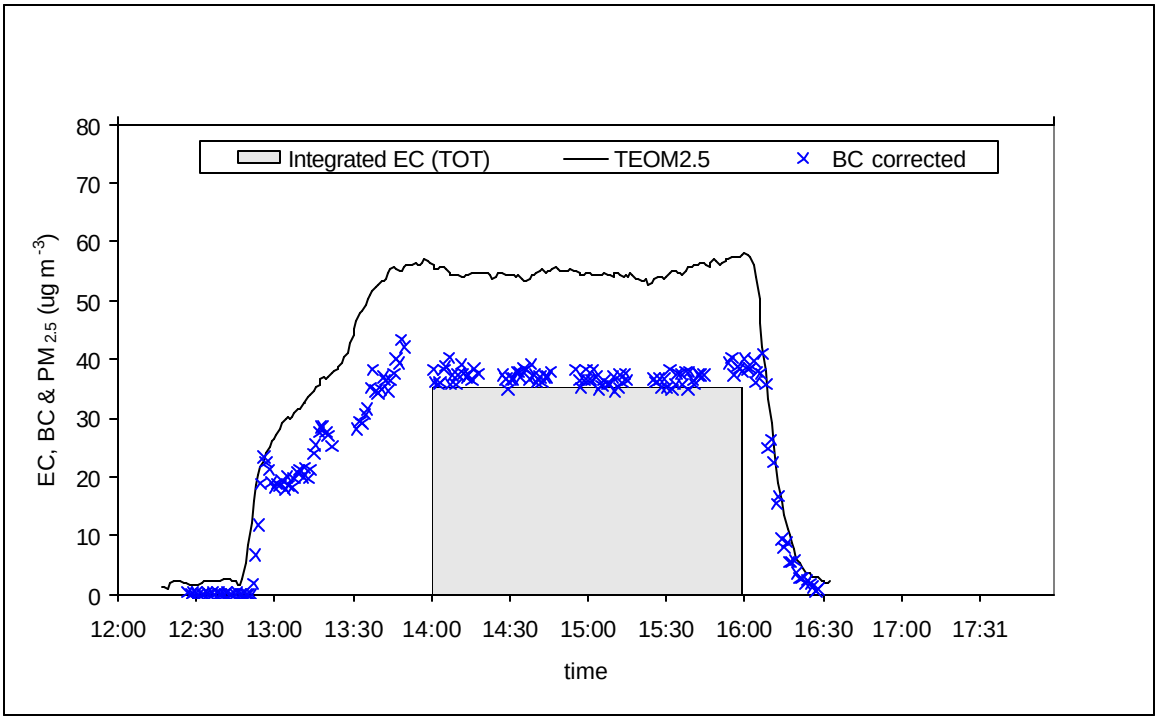

Figure 6. Proposed algorithm applied to the aethalometer in order to measure near real-time concentration of BC from fresh Diesel soot.

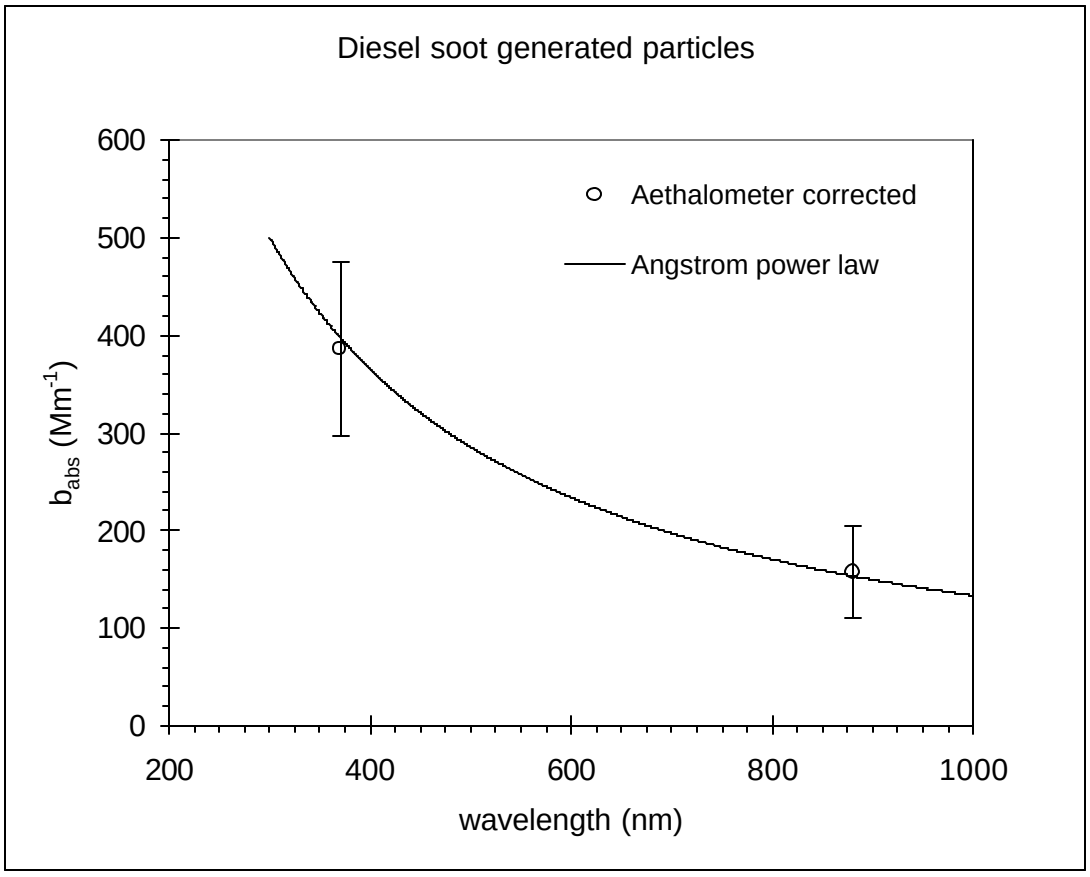

Figure 7. Wavelength dependence comparison of the experimentally determined absorption coefficient b_{abs} using the aethalometer. The aethalometer b_{abs} is corrected for loading effect K(ATN) and multiple scattering effect, C of the filter matrix. The solid line represents the fitting of the reference b_{abs} determined using the Ångström power law, $b_{abs} = ?^{-a}$ with a =1.1 for Diesel soot extracted from Schnaiter et al. (2003).

CHAPTER 5: SUMMARY AND CONCLUSIONS

The preceding chapters underline relevant aspects of aerosol characterization for smoke from agricultural field burning of wheat and Kentucky bluegrass (KBG) residues. This encompasses the comprehensive objective of improving the understanding of air quality impacts from regional field burning in the populated areas of eastern Washington and northern Idaho, specifically particulate matter pollution, which is known to have detrimental effects on human health from chronic and acute exposure (US EPA, 2004), and also leads to low visibility (Crutzen and Andrae, 1990). The approach used to quantify air pollution from regional field burning was measuring and monitoring $PM_{2.5}$ (particulate matter less than 2.5 μm in aerodynamic diameter) concentrations in populated areas during periods of prescribed field burning. This involved deploying monitors able to measure $PM_{2.5}$ concentration directly (gravimetric methods) or indirectly, through the light scattering properties of aerosols (e.i., nephelometer). However, it was shown through receptor modeling that in addition to smoke from field burning, this semi-arid region, had significant amounts of particles in the air from other sources, which may include fugitive dust from roads and adjacent fields, 38% of the total $PM_{2.5}$ mass concentration, whereas the PM contribution from vegetative burning was approximately 35% of the observed $PM_{2.5}$ in Pullman, WA in the fall of 2002.

The use of receptor models, such as the US EPA Chemical Mass Balance (CMB) receptor model (Watson et al., 2001) was proven to be effective in apportioning $PM_{2.5}$ from vegetative burning among other common sources of PM in the area (e.i. airborne soil) by including the specific molecular tracer levoglucosan (LG), a marker for cellulose

combustion (Simoneit, 2002). The distinction between dust and vegetative burning originated $PM_{2.5}$ was necessary, because this information provided the base for the more comprehensive study examining community exposure to agricultural burning smoke and the related health effects.

However, levoglucosan alone was not as effective in apportioning aerosols emitted from combustion of agricultural residues, when other sources of vegetative burning aerosols may affect the region. In the Pullman study we found a significant correlation ($r= -0.6$, $p<0.01$) between LG and ambient temperature, which could be attributed to residential wood burning, as ambient temperatures decreased later in the fall. Moreover, we have documented substantial air pollution events in urban areas of eastern Washington and northern Idaho linked to wildfires in the region (Jimenez, 2000), which could also affect the ability of apportioning air pollution from agricultural field burning through source receptor modeling.

Selecting specific markers for apportioning PM pollution from agricultural field burning in the area was important, since the performance of the CMB model directly depends on the quality, authenticity and uniqueness of the tracers selected to identify a particular source. We learned that the lignin content and chemical structure varies with plant species (Ibrahim, 1998; Simoneit, 2002), and that lignin pyrolysis products (methoxyphenols) are important compounds in smoke from biomass combustion (Simoneit et al, 2000). Therefore, we targeted 19 methoxyphenols (MP), and the relative proportion (relative to $PM_{2.5}$ mass) of these compounds was used to distinguish agricultural residue smoke from smoke derived from hardwood combustion. Comparisons between these markers present in smoke from wheat and KBG stubble

burning, collected in chamber and field experiments, showed that the amount of total MPs found in wheat stubble smoke was higher (>2 times) than similar amounts found in KBG smoke. Additionally, syringaldehyde, acetosyringone and coniferylaldehyde were found to be the most prominent particle-phase tracers (among the analyzed MPs) for wheat stubble smoke, and these compounds were not always present in detectable amounts in KBG smoke, and these MPs are also present in considerable amounts in hardwood smoke. Therefore, we proposed to consider these prominent MPs relative to the amounts of LG found in $PM_{2.5}$ from smoke. The ratio LG/ syringaldehyde was found much higher in wheat (~80) than similar ratios reported for hardwood (~5) (Fine et al., 2001; Fine et al., 2002; Hays et al., 2002). Similarly, smoke from softwood has a low ratio (~7) of LG/ coniferylaldehyde compared to wheat stubble smoke (~180) due to the higher content of coniferylaldehyde in wheat smoke relative to the levoglucosan content.

Ideally, the relative proportions of these organic tracers (MPs and LG) in PM from smoke should be more or less constant for a particular type of crop residue combustion. However, it was found that the relative proportion of the MPs in the field collected samples from wheat stubble smoke were lower than similar compounds measured in $PM_{2.5}$ collected in the chamber, with the exception of two syringol compounds (syringaldehyde and acetosyringone) that were higher in the field samples compared to chamber samples. One possible explanation may be enhanced volatilization of methoxyphenols from particles in the field experiment, or changes in the particle phase - vapor phase equilibrium upon temperature and vapor pressure during sampling, bearing in mind that these MPs are also present in important amounts in the vapor phase.

Additionally, photochemical degradation and transformation of methoxyphenols has been previously documented (Hawthorne et al., 1992). Hawthorne and co-authors noted that the relative amounts of syringaldehyde and acetosyringone were enhanced in ambient PM samples compared to PM collected directly from fireplace chimneys. The authors speculated that this enhancement may be due to oxidative transformation of other syringyl-type MPs into syringaldehyde and acetosyringone. A similar mechanism may explain our observation of an apparent increase in the relative concentrations of syringaldehyde and acetosyringone in the field samples compared to the chamber samples, while relative concentrations of the other syringyl derivatives were reduced.

This mechanism of methoxyphenol transformations should be considered when apportioning $PM_{2.5}$ pollution from field burning at a given receptor location through CMB modeling. If the profiles used for distinguishing PM emitted during farm field burning includes lignin pyrolysis products (MPs) they should consider enrichment/ degradation of these compounds in the atmosphere, as well as during collection and analysis. More work is required for understanding these transformation processes in the atmosphere during transport and dispersion downwind of the fire. This information could be used in receptor models by adjusting the relative proportions of methoxyphenolic compounds in the profiles to conditions of photochemistry and transport time to a particular receptor site.

On the other hand, one of the main goals of the comprehensive study examining community exposure to field burning smoke was to quantitatively measure negative health effects on a selected group of people from exposure to agricultural burning smoke. For this reason, trends in the continuous $PM_{2.5}$ concentration measurements from either

TEOM or nephelometer were monitored, and potential smoke episodes (requiring a more intensive human subject testing) were declared when three or more consecutive 30-min averaged values exceeded 40 μm m^{-3}, a threshold value selected from our previous study linking $PM_{2.5}$ concentrations to air pollution episodes from agricultural field burning (Jimenez, 2000). However, it was found that for the fall 2002 study, the continuous $PM_{2.5}$ measurements alone were not able to distinguish vegetative combustion from soil originated PM, and filter-based $PM_{2.5}$ samples collected over time (12-hr) did not capture short-term variations nor was feasible to analyze the PM samples for tracers and run models.

While knowing that biomass burning emits light absorbing carbon (LAC) into the atmosphere, near real-time concentrations of LAC can be measured using the aethalometer. The aethalometer is a semi-continuous instrument that measures black carbon (BC) aerosol concentrations from its light absorption properties through a quartz filter (Hansen et al., 1984). Nonetheless, evidence indicates that quartz fiber filters are prone to absorb semi-volatile organic compounds (SVOC's) (Eatough et al., 1995; Pang et al., 2002) and this may interfere with the aethalometer measurements. Additionally, two optical interferences due to the multiple scattering and the accumulation of highly absorbing particles in the filter matrix have been reported for this instrument (LaRosa et al., 2002; Weingartner et al., 2003). Therefore, we needed to further investigate the operational principle of this instrument, its capabilities and limitations prior to being used for near real-time mornitoring of air prolution from biomass burning.

As a way of understanding the effects of semi-volatile organic compounds on the optical absorption of this instrument, we designed an experiment with controlled

conditions of PM from Diesel exhaust. For this purpose we equipped one of the aethalometers with a SVOC denuder, and we observed on average a 13% reduction in the denuded aethalometer measurements, while thermal optical evolved gas analysis from collocated samples showed that this reduction was mainly at the most volatile fractions of organic carbon.

In addition, we developed a procedure for correcting the current aethalometer algorithm that is capable of providing more reliable measurements of real-time high concentrations of BC from Diesel exhaust. This correction included a parametrization of a so-called "loading effect", which required fixing the concentrations of light absorbing PM to a relative stable value for an extensive period of time. In this experiment, we used a specially designed chamber capable of actively maintaining constant concentrations of $PM_{2.5}$ from Diesel exhaust, and we scaled the aethalometer optical absorption measurements of LAC to elemental carbon concentrations determined from thermal optical analysis using an established protocol for determining the split between organic carbon (OC) and elemental carbon (EC) (NIOSH 5040). However, interlaboratory analyses of carbonaceous aerosol samples have shown that EC and/or BC estimates vary considerably depending upon the method and protocol used for analysis (Countess, 1990; Shah and Rau, 1991; Schmid et al., 2001, Watson et al., 2005). Furthermore, results from the analysis of a reference material by different thermal optical methods yield a wide range of EC estimates (Currie et al., 2002; Klouda et al., 2005). Clearly there is a large uncertainty in EC and/or BC measurements due to the lack of agreement between the standardized methods for analysis.

Further work should include more research focused on reducing these uncertainties by developing a more robust method for measuring carbonaceous aerosol concentrations, in particular EC. This involves developing and testing new standards and/or reference material for instrument calibration. Finally, the proposed approach for correcting the aethalometer should be tested with aerosols emitted from field burning combustion, mixed aerosol, including non-absorbing aerosols, as well as in ambient air with diesel exhaust and environmental tobacco smoke.

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