

# **EPA Public Access**

Author manuscript

Atmos Environ (1994). Author manuscript; available in PMC 2020 July 01.

About author manuscripts

Submit a manuscript

# Published in final edited form as:

Atmos Environ (1994). 2017; 166: 22-33. doi:10.1016/j.atmosenv.2017.06.043.

# Emissions from prescribed burning of agricultural fields in the Pacific Northwest

A.L. Holder<sup>a</sup>, B.K. Gullett<sup>a</sup>, S.P. Urbanski<sup>b</sup>, R. Elleman<sup>c</sup>, S. O'Neill<sup>d</sup>, D. Tabor<sup>a</sup>, W. Mitchell<sup>a</sup>, K.R. Baker<sup>e</sup>

<sup>a</sup>U.S. Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Research Triangle Park, NC 27711, USA

<sup>b</sup>U.S. Forest Service, Missoula Fire Science Laboratory, Rocky Mountain Research Station, 5775 US Hwy 10W, Missoula, MT 59808, USA

<sup>c</sup>U.S. Environmental Protection Agency, Region 10, Seattle, WA 98101, USA

<sup>d</sup>U.S. Forest Service, Pacific Northwest Research Station, 400 N 34th, St. Suite 201, Seattle, WA 98103, USA

<sup>e</sup>U.S. Environmental Protection Agency, Office of Air Quality Planning & Standards, Research Triangle Park, NC 27711, USA

# Abstract

Prescribed burns of winter wheat stubble and Kentucky bluegrass fields in northern Idaho and eastern Washington states (U.S.A.) were sampled using ground-, aerostat-, airplane-, and laboratory-based measurement platforms to determine emission factors, compare methods, and provide a current and comprehensive set of emissions data for air quality models, climate models, and emission inventories. Batch measurements of PM2.5, volatile organic compounds (VOCs), polycyclic aromatic hydrocarbons (PAHs), and polychlorinated dibenzodioxins/dibenzofurans (PCDDs/PCDFs), and continuous measurements of black carbon (BC), particle mass by size, CO, CO2, CH4, and aerosol characteristics were taken at ground level, on an aerostat-lofted instrument package, and from an airplane. Biomass samples gathered from the field were burned in a laboratory combustion facility for comparison with these ground and aerial field measurements. Emission factors for PM2.5, organic carbon (OC), CH4, and CO measured in the field study platforms were typically higher than those measured in the laboratory combustion facility. Field data for Kentucky bluegrass suggest that biomass residue loading is directly proportional to the  $PM_{25}$  emission factor; no such relationship was found with the limited wheat data.  $CO_2$  and BC emissions were higher in laboratory burn tests than in the field, reflecting greater carbon oxidation and flaming combustion conditions. These distinctions between field and laboratory results can be explained by measurements of the modified combustion efficiency (MCE). Higher MCEs were recorded in the laboratory burns than from the airplane platform. These MCE/emission factor trends are supported by 1–2 min grab samples from the ground and aerostat platforms. Emission factors measured here are similar to other studies measuring comparable fuels, pollutants, and

Publisher's Disclaimer: Disclaimer

Publisher's Disclaimer: The views expressed in this publication are those of the authors and do not necessarily represent the views or policies of the U.S. Environmental Protection Agency.

combustion conditions. The size distribution of refractory BC (rBC) was single modal with a lognormal shape, which was consistent among fuel types when normalized by total rBC mass. The field and laboratory measurements of the Angstrom exponent ( $\alpha$ ) and single scattering albedo ( $\omega$ ) exhibit a strong decreasing trend with increasing MCEs in the range of 0.9–0.99. Field measurements of  $\alpha$  and  $\omega$  were consistently higher than laboratory burns, which is likely due to less complete combustion. When VOC emissions are compared with MCE, the results are consistent for both fuel types: emission factors increase as MCE decreases.

# Graphical abstract



#### Keywords

Agricultural burning; Emission factors; Wheat; Bluegrass; Particulate matter; Organics

# 1. Introduction

The Pacific Northwest is a notable agricultural region. Seventy-five percent of U.S. grass seed farms are located in Idaho, Oregon, and Washington (Wulfhorst et al., 2006). This region also accounts for roughly 25% and 10% of total U.S. acreage for barley and wheat, respectively (U.S. Department of Agriculture, 2015). Crop residue burning is a widely used agricultural management tool in the contiguous United States as a low-cost method for reducing residue and controlling or eliminating fungal diseases, pest eggs, and weeds (Kumar and Goh, 1999, McCarty et al., 2009, McCarty, 2011). Burning provides the additional benefit of ash fertilization by quickly recycling minerals back to the soil (McCarty, 2011). In the Pacific Northwest, cereals (e.g., wheat and barley) and grass seed (e.g., Kentucky bluegrass) are the crop types most commonly managed with fire (Hart et al., 2012). Direct seeding of cereal crops often includes crop residue burning to reduce or

eliminate tillage prior to seeding and thereby helps maintain soil quality and reduce erosion (Air Sciences Inc, 2003, Huggins, 2005). However, direct seeding in heavy residues requires specialized and expensive machinery (Air Sciences Inc, 2003, Huggins, 2005). Residue removal through burning can reduce the costs of direct seeding while providing the aforementioned benefits.

One disadvantage to agricultural field burning is the emissions of particulate and gaseous pollutants that can impact local and regional air quality as well as impact inhalation exposures. An estimated ~1.2 million ha of croplands are burned annually on average in the continental United States (McCarty et al., 2009). Along with the Southeast and the Great Plains, the Pacific Northwest is a region of major agricultural burning, with cropland burning of nearly 200,000 ha per year (McCarty et al., 2009). In response to citizen complaints, litigation, and state legislative action, state and tribal agencies strictly manage smoke from field burning in the Pacific Northwest (SAFE AIR FOR EVERYONE v. MEYER, 2004, SAFE AIR FOR EVERYONE v. U.S. EPA, 2007, Seattlepi, 2003, Spokesman-Review, 2005, Wulfhorst et al., 2006). A challenge to reducing smoke impact has been to accurately predict smoke production and dispersion over the range of atmospheric conditions and burn scenarios encountered in the region (Jain et al., 2007). These predictions critically rely on limited emission factor data for agricultural burning (Pouliot et al., 2016).

Two previous large field studies of emissions from agricultural burning in the Pacific Northwest provide a comparison with our results. The studies measured meteorological variables, fuel characteristics, and emission factors (PM2.5, CO2, CO, CH4, and six PAHs) for open field burns with the primary aim of identifying PM<sub>2.5</sub> emission reduction strategies for the burning of post-harvest residue (Air Sciences Inc, 2003, Johnston and Golob, 2004). More recent laboratory simulations have provided additional information about the composition of emissions from agricultural burning (Dhammapala et al., 2006, Dhammapala et al., 2007b, Jain et al., 2007, Johnston and Golob, 2004). The study reported here builds upon these past studies by providing comprehensive measurements of particulate matter and gas phase composition of emissions from agricultural burning using multiple measurement platforms. These measurements were made on emissions from the burning of winter wheat and Kentucky bluegrass fields in northern Idaho and eastern Washington. Measurements of smoke were taken near and downwind of multiple prescribed fires in the Pacific Northwest region to provide information to evaluate and improve the representation of smoke impact in air quality modeling systems such as Washington State University's ClearSky (Jain et al., 2007), Airpact (Vaughan et al., 2004), and photochemical grid models used for regulatory assessments (Baker et al., 2016). Fuel characteristics were measured before field burning. Fresh emissions were measured at ground-level, with an aerostat-lofted instrument package, and from a fixed-wing airplane to provide multiscale emissions information. Comparison of these spatially variant measurements whether sampling location or method introduced a bias from, for example, disproportionate sampling of smoldering emissions. Fuels from the field study were also burned in a controlled laboratory facility to provide another estimate of emission factors for comparison with the field-based estimates. These findings are compared with results from previous field experiments and with recent, more extensive laboratory studies.

# 2. Methods

#### 2.1. Biomass and site description

Four fields of Kentucky bluegrass (*Poa prantensis* L., "KBG") in Idaho and four fields of winter wheat (*Triticum aestivum* L., "wheat"), one in Idaho and three in Washington state, were burned (Table 1) in late summer (August) for this field study. The KBG fields represented a range of fuel loadings (determined by oven drying), including one field that was baled. Crop yields were lower than normal in the year we conducted our study, so the high end of KBG and wheat fuel loadings may not be adequately represented here. All of the Washington wheat fields had been treated with herbicide, then left dormant ("chem-fallow"). The biomass (e.g., wheat or KBG) was generally homogeneous across each individual unit selected for burns. Quantities of the raw biomass were gathered immediately prior to ignition and stored in tied plastic bags for subsequent laboratory burn tests. The biomass was weighed in the field using a portable balance and later oven dried for moisture determination on a dry weight basis. Further details on field location and biomass sampling methods are included in Treesearch (USFS, https://www.treesearch.fs.fed.us/pubs/pending). Each biomass type was tested in the laboratory Open Burn Test Facility (OBTF) under procedures described more fully elsewhere (Aurell and Gullett, 2013).

# 2.2. Ground and aerostat instrumentation and sampling methods

Similar instrumentation packages, each termed the "Flyer" (SI Fig. S1, discussed fully elsewhere (Aurell and Gullett, 2010, Aurell and Gullett, 2013, Aurell et al., 2012)), were used on the ground and on the helium-filled aerostat. Briefly, the Flyer was maneuvered into the plume at an average height of 50 m using a 4.3 m diameter aerostat (Kingfisher Model, Aerial Products Inc., USA) tethered to an all-terrain vehicle (ATV) with an electric winch. A second, ground-based Flyer was mounted on the back of an ATV atop a sampling platform (2.5 m height). Measurements on board the Flyers are detailed in Table 2. Two simultaneous PM<sub>2.5</sub> samples were gathered at a constant airflow (10 L/min) using Teflon filters for PM mass and quartz filters for elemental carbon (EC), organic carbon (OC), and total carbon (TC). The EC, TC, and OC were analyzed via a modified, thermal-optical analysis (TOA) (Khan et al., 2012, National Institute for Occupational Safety and Health, 2016). Volatile organic compounds (VOCs), as well as CO2 and CO, were sampled using SUMMA Canisters (Columbia Analytical Services - CAS, U.S.A.). Additional details about PAHs (Aurell and Gullett, 2010) and other analysis procedures are available elsewhere (Aurell and Gullett, 2013). Field blanks were collected and analyzed for polychlorinated PCDDs/ PCDFs, PAHs, PM2.5, EC, OC, TC, and VOCs. Background values for continuous measurements were determined immediately before the burns. All concentrations were blank or background subtracted to determine the excess mixing ratio. All ground instruments were time-synchronized each day to a GPS clock. All instruments were calibrated following procedures detailed elsewhere (Aurell and Gullett, 2013). The LiCOR CO<sub>2</sub> system underwent a daily pre- and post-sampling three-point calibration according to U.S. EPA Method 3A (U. S. Environmental Protection Agency, 2016).

# 2.3. Aerosol optical instrumentation and sampling methods

Measurements of aerosol light absorption, scattering, and refractory black carbon (rBC) mass (Table 2, "Ground aerosol optical measurements") were performed on the ground near the ATV-mounted Flyer and are described in detail elsewhere (Holder et al., 2016). A portable aerosol dilution system (Grimm DIL 550) was used with the Single Particle Soot Photometer (SP2) in the field to reduce the number concentration of refractory black carbon into the instrument's range. For SP2 measurements in the OBTF (described later), a series of dilution systems (Palas VKL 10) was used with zero air as a dilution gas to provide a user-regulated dilution ratio from 10:1 to 350:1. In addition to the aerosol optical properties, collocated measurements of PM<sub>2.5</sub>, EC, OC, TC, CO<sub>2</sub>, and equivalent black carbon (eBC) were made identical to those on the Flyer. eBC is derived from filter-based attenuation measurements using the manufacturer's mass-specific absorption coefficient, and rBC is based on thermal emission of particulate carbon absorbing laser energy (Petzold et al., 2013).

#### 2.4. Airplane instrumentation and sampling methods

The airplane measurement platform was a Cessna 206. Smoke and ambient air were sampled through a 5.1 cm ventilation inlet located on the passenger side wing. A flight-ready cavity ring-down spectroscopic (CRDS) trace-gas analyser (Table 2) was used to take continuous measurements of CO<sub>2</sub>, CO, and CH<sub>4</sub> with a data acquisition frequency of 2 s (Urbanski, 2013). In-flight, triple point calibrations using National Institute of Standards and Technology (NIST)-traceable standards were used to ensure accuracy of the CRDS measurements and quantify the measurement precision. A nephelometer sampled air downstream of a cyclone with a 2.5 µm cut point measuring integrated light scattering (b<sub>scat</sub>) at 530 nm (Table 2, "Airplane: Cessna-206 measurements"). After the field campaign, the measurements of b<sub>scat</sub> by the nephelometer were calibrated with gravimetric measurements of PM<sub>2.5</sub> mass by a series of burns in the US Forest Service Missoula combustion facility. We estimate the uncertainty in the "inferred"  $PM_{2.5}$  measurements is ~50%. Details of the nephelometer calibration and uncertainties in the "inferred" PM2.5 are provided in the Supporting Information. The CRDS and nephelometer instruments pulled approximately 0.5 standard L/min and 16.7 standard L/min off the sample line, respectively. The excess sample flow and the CRDS and nephelometer outflow were exhausted out the rear of the fuselage through a 1.27 cm o.d. Teflon line. Measurements of fresh emissions were obtained with parallel flight transects roughly perpendicular to the long axis of the smoke plume, taken at multiple altitudes. Emissions were determined from level-altitude flight segments that began in smoke-free background air, passed through the smoke plume, and then re-entered the background air. A section of each flight segment prior to plume entry provided the background measurements that were used to calculate the excess mixing ratios. The background CO provided a baseline to identify the smoke plume entry and exit points and selection of the smoke sample data points.

# 2.5. Open Burn Test Facility

To simulate prescribed burning of agricultural fields, a 70 m<sup>3</sup> enclosed, ventilated laboratory OBTF (Grandesso et al., 2011) was used to combust the biomass and measure sample

emissions. In summary, a high-volume blower pulls ambient air to the OBTF and together with small fans located inside the facility ensures complete mixing and oxygen concentrations close to ambient throughout the burn. The fuel charge size (0.5 kg) was spread on the burn pan to mimic the fuel density in the fields (0.58 kg/m<sup>2</sup>). Biomass was burned on sand atop an aluminum-foil-covered steel plate (0.93 m × 0.93 m). To minimize the possibility of non-detectable PCDD/PCDF congeners, emissions from multiple burns were composited using two Flyer samplers in parallel to obtain one PCDD/PCDF sample. The same sampling instruments were used in the OBTF as in the field with the addition of a carbon monoxide (CO) continuous emission monitor. Ambient air background samples were collected inside the OBTF after sampling to include both ambient levels and any potential facility wall contamination.

## 2.6. Data analysis

A carbon mass balance approach (Ward et al., 1979) was used to derive emission factors (EFs) using simultaneous measurements of pollutant mass and carbon species along with the carbon fraction in the biomass. For KBG, wheat, and chem-fallow wheat, the carbon fractions were 0.44, 0.44, and 0.42, respectively, based on an ultimate analysis of the biomass. Only CO2 was measured continuously in the field with the ground- and aerostatbased instruments due to weight and power limitations, while both CO<sub>2</sub> and CO were measured in the OBTF and airplane. On average, the EFs in this study were  $3.8\% \pm 2.0\%$ lower using CO<sub>2</sub> and CO as the carbon source rather than only CO<sub>2</sub>. Ground- and aerostatbased grab sample measurements using canisters include both CO and CO2 in the EF calculations. The Modified Combustion Efficiency (MCE), a measure of a fire's flaming versus smoldering combustion, was calculated by dividing  $CO_2$  with (  $CH_4 + CO +$  $CO_2$ ), where  $CO_2$ , CO, and  $CH_4$  are the mixing ratio enhancements of these gases above background. MCE provides a metric to subjectively describe fires as flaming (MCE > (0.95) or smoldering (MCE < 0.90). Many species produced in biomass burning are predominantly emitted during either flaming or smoldering combustion (Burling et al., 2010, Yokelson et al., 1996). Since MCE characterizes the relative mix of flaming and smoldering combustion, the emission factors were analyzed to identify correlations with MCE. The eBC data from the AE51 were post-processed using an optimizing noise-reduction averaging algorithm program (Hagler et al., 2011). The eBC data were not corrected for particle loading on the filters since the eBC concentration did not change with an increased optical attenuation. Data were analyzed using an analysis of variance (ANOVA) method.

The toxic equivalent factors, TEFs (Larsen and Larsen, 1998), and the 2005 World Health Organization (WHO) TEFs (Van den Berg et al., 2006) were used to determine the PAH toxicity equivalent quotient, TEQ (B[a]P-TEQs) and PCDD/PCDF TEQ values, respectively. Non-detectable TEF-weighted PCDD/PCDF congeners were set to zero. Filter-based gravimetric measurements of  $PM_{2.5}$  during laboratory burns of biomass collected from the fields were used to develop a linear relationship relating  $b_{scat}$  to  $PM_{2.5}$  mass concentration. The relationship is valid only for fresh smoke samples and since  $b_{scat}$  is determined by particle properties not measured (e.g., size distribution and chemical composition), we consider the derived quantity as "inferred"  $PM_{2.5}$ .

# 3. Results and discussion

#### 3.1. General emissions

Fig. 1 shows EFs for the sampling platforms for both KBG and wheat. EFs are determined for  $PM_{2.5}$  as well as  $PM_{2.5}$ -associated OC, EC, and eBC. These data are enumerated in Table 3 along with TC and MCE values for the airplane and OBTF. These emission factors were derived from analysis of the  $PM_{2.5}$  impactor filters and cover the period of time until the pressure drop indicated plugged filters. The average sampling time was 30 min, reflecting the full range of both active flaming and smoldering conditions but omitting the subsequent residual smoldering stage.

 $PM_{2.5}$  emission factors for wheat and KBG ranged between 10 and 20 g/kg biomass burned except for the OBTF testing and the airplane/wheat values where values were below 10 g/kg. Both the OBTF and airplane emission factors are significantly different (lower) than the ground and aerostat values (p-value = 0.0001, F = 23.0). For the airplane and the OBTF, the lower  $PM_{2.5}$  values appear to be associated with high MCE values (Table 3). Indeed, the airplane  $PM_{2.5}$  emission factors were lower for wheat where the MCE was highest (0.96 vs. 0.93 for KBG). No statistical difference was found between the wheat and the chem-fallow wheat  $PM_{2.5}$  emission factors.

The OBTF may have higher MCE values than the values from the field determinations due to drying of the biomass, although care was taken to bag the samples in the field securely to avoid moisture loss. The lower  $PM_{2.5}$  values for the airplane contrast with the aerostat and ground data and may partially result from dilution-driven evaporation of organic aerosol (May et al., 2015), although uncertainty in the inferred  $PM_{2.5}$  measurement cannot be ruled out. The nephelometer calibration, which was conducted in the laboratory, depends on particle size and composition, which may change during plume dilution and also may not be comparable if the laboratory burns had a different mixture of flaming and smoldering than that seen in the lofted plume. Therefore, the ground and aerostat measurements provide the most relevant  $PM_{2.5}$  EFs.

Liu et al. (2016) measured a PM<sub>1</sub> emission factor of  $15.4 \pm 7.1$  g/kg for rice straw burning, in agreement with our ground and aerostat measurements for both KBG and wheat residues. A previous laboratory study in the OBTF (Dhammapala et al., 2006) measured PM<sub>2.5</sub> emission factors for KBG of 12 g/kg (MCE = 0.90) and wheat of 3 g/kg (MCE = 0.95); the latter is lower than our ground and aerostat platforms but consistent with the airplane estimates.

EC emissions were approximately the same for the wheat and KBG. Ground values were a bit lower than other platforms. Emission factors were within the range observed in the field study by Dhammapala et al. (2007b) of 0.15-1.09 (g/kg) but generally larger than observations from rice straw (Liu et al., 2016) of  $0.167 \pm 0.14$  (g/kg). OC emission factors across both biomass types and all platforms, averaged  $8.8 \pm 4.7$  g/kg. This value is much greater than those for EC, as is common to open burning of biomass. There is some evidence that the OC was subject to a positive artifact (Subramanian et al., 2004) as the TC was greater than the PM2.5 EF for the KBG Aerostat sampling platform. EC and eBC emission

factors, averaged over all platforms and biomass types, were  $0.5 \pm 0.2$  g/kg and  $0.8 \pm 0.3$  g/kg, respectively, and fall within the range estimated elsewhere for prescribed forest and grassland burns (Aurell et al., 2015).

#### 3.2. Aerosol optical characteristics

The burn-averaged aerosol optical properties including Angstrom exponent ( $\alpha$ ) and single scattering albedo ( $\omega$ ) are shown in Table 4. The  $\alpha$  has been used as an indicator of brown carbon and along with  $\omega$ , are atmospheric absorbance and reflectivity parameters (Holder et al., 2016). Higher a values (>2) indicate the presence of brown carbon which absorbs at shorter wavelengths than BC. Brown carbon likely impacts the aerosol radiative force and leads to a reduction in photochemistry and subsequent ozone production (Laskin et al., 2015). Higher  $\omega$  values imply a more scattering aerosol, which can lead to a cooling effect. Optical properties were measured for only two burns for each fuel type in the field, so there were insufficient data to confirm emission dependencies on fuel type or MCE for the field burn samples. A positive linear correlation with fuel loading was observed for  $\omega$  (r<sup>2</sup> = 0.7) for all fuel types, but not with a  $(r^2 = 0.03)$ . There was a statistically significant difference (p < 0.01 ANOVA) between  $\omega$  and  $\alpha$  for the same fuels burned in the field compared with the OBTF. In the OBTF,  $\omega$  and  $\alpha$  were consistently lower than the values measured in the field. Since the MCE was consistently higher in the OBTF compared to the field, the varying optical properties were likely due to differing combustion conditions in the OBTF versus the field. There was no statistically significant difference of either  $\alpha$  or  $\omega$  with the fuel type for the OBTF burns.

When the field and OBTF data are combined,  $\alpha$  increases exponentially with increasing  $\omega$ , agreeing with biomass burning emissions in laboratory conditions (Lewis et al., 2008, Liu et al., 2014, McMeeking et al., 2014). There was a linear decrease in  $\omega$  with increasing EC to TC ratio ( $r^2 = 0.80$  in field,  $r^2 = 0.68$  all data), showing that EC (or BC) is the primary absorber at 532 nm. There was no clear relationship between  $\alpha$  and EC to TC ratio ( $r^2 = 0.25$ ) for these field burns, which showed similar  $\alpha$  values despite a spread of EC to TC ratios from 0.005 to 0.058. However, inclusion of the OBTF burns shows a trend of increasing  $\alpha$  with decreasing EC to TC ratio ( $r^2 = 0.52$ ), similar to the exponential increase in  $\alpha$  with decreasing rBC fraction seen for laboratory biomass burns by others (McMeeking et al., 2014).

Very few measurements of aerosol optical properties of fresh emissions from wildland fires are available for comparison and to our knowledge, there are no published measurements of aerosol absorption for emissions from in-field burning of KBG or wheat residues. In a previous study using the same experimental approach, an  $\omega$  (550 nm) of 0.83 and  $\alpha$  (405– 781 nm) of 2.4 were measured for a prescribed burn of grasslands in Florida (Holder et al., 2016). Liu et al. (2016) measured an  $\alpha$  (532–470 nm) of 3.34 ± 0.62 for airborne measurements of fresh emissions from rice straw burning, which is similar to the  $\alpha$  observed for the field wheat straw burns, despite the different fuel and measurement method. Abel et al. (2003) measured a  $\omega$  (550 nm) of 0.83 for agricultural burning in Africa. Reid and Hobbs (1998) measured substantially lower  $\omega$  (550 nm) of 0.76 ± 0.08 for grassland fires in Brazil. Laboratory measurements have also exhibited substantially lower  $\omega$  and  $\alpha$  than these in-field

burns. For example, Liu et al. (2014) observed  $\omega$  (532 nm) of 0.78 ± 0.17 and  $\alpha$  (405–781 nm) of 1.95 ± 0.65 for wheat straw taken from various locations in the U.S. These large differences between our field and OBTF measurements and those other studies come into better agreement when compared on the basis of MCE (Fig. 2). Both  $\alpha$  and  $\omega$  exhibit a strong decreasing trend with increasing MCEs in the range of 0.9–0.99 (Liu et al., 2014). The field measurements and OBTF measurements exhibit the same relationship with MCE suggesting that the  $\omega$  parameterization as a function of MCE developed by Liu et al. (2014) is valid for fresh emissions from in field burning of agricultural residues.

## 3.3. rBC size distributions

Mass median diameters  $(D_m)$  and geometric standard deviations  $(\sigma_g)$  for the burn-averaged rBC mass weighted size distributions are shown in Table 4. All rBC size distributions exhibited a lognormal shape (Fig. S2) with a single mode that when normalized by total rBC mass concentration were similar across fuel types, despite varying mass concentrations and dilution conditions. The rBC emissions from KBG burned in the OBTF had statistically significant larger  $D_m$  (173 nm ± 4 versus 165 nm ± 1, p = 0.03) and smaller  $\sigma_g$  (1.46 nm ± 0.01 versus 1.49 nm ± 0.01, p = 0.004) than rBC from KBG burned in field. No comparison could be made for either wheat or chem-fallow wheat because of the small number of field burns measured. There was no statistically significant difference in  $D_m$  by fuel type for the OBTF burns. Overall, the differences in the rBC size distribution among the different field burns were small and likely less than the uncertainty in the rBC mass measurement. The uncertainty in the rBC mass measurement could not be quantified due to the uncertain applicability of the SP2 calibration material (fullerene soot) to emissions from agricultural residue burning.

The rBC size distributions from these agricultural residues were similar to emissions from grassland fires ( $D_m = 174$  nm) in Florida but much smaller than those observed from a fire on forested land ( $D_m = 209 \text{ nm}$ ) (Holder et al., 2016). Other measurements of rBC size distributions from wildland fires have been mainly from forested areas in North America. D<sub>m</sub> values of 190 nm for a boreal forest in Canada (Kondo et al., 2011), 220 nm for a temperate forest in South Carolina (May et al., 2014), and 210 nm for brush land in Texas (Schwarz et al., 2008) have been observed. Sahu et al. (2012) measured  $D_m$  at 200 nm over parts of California that may have resulted from agricultural burning. However, without detailed information of the fuels burned in these fires, it is difficult to determine if the rBC size distribution depends on fuel type or combustion conditions. May et al. (2014) measured rBC size distributions of biomass fuels burned in the laboratory, but found no clear dependence on fuel type or on MCE. However, they observed much larger rBC sizes in South Carolina (220 nm) wildland fires compared to the average of similar fuels burned in the laboratory (170 nm), suggesting that conditions in laboratory burns may not accurately mimic the rBC size distribution emitted from wildland fires. We did not see such a large difference between the field and OBTF rBC size distributions for agricultural residues, so this lack of agreement may be limited to the larger scale forest fuels. These shifts in size distribution that may occur by fuel type are important as the size distribution of rBC and PM govern their atmospheric lifetime, the ability to act as cloud condensation nuclei, and radiative impact (Winijkul et al., 2015).

# 3.4. PAHs and PCDD/PCDF

Emission factors for 16 gas and particle phase PAHs are shown in Table 5. The average field emission factors for the sum of the 16 PAHs were 53 and 33 mg/kg for KBG and wheat, respectively. The emission factors from the OBTF were substantially lower than those from the field, most prominently for KBG, 15 versus 53 mg/kg. These biomass and field/OBTF results both may be relatable to MCE, where higher MCE values are associated with lower combustion byproducts. Of all these emission factors, only the average, TEF-weighted KBG emission factor from the field (0.49 mg B[a]P-TEQ/kg) is similar to previously reported laboratory tests with KBG at 0.58 mg B[a]P-TEQ/kg and wheat at 0.64 mg B[a]P-TEQ/kg (Dhammapala et al., 2007b). The average wheat emission factor (0.20 mg B[a]P-TEQ/kg) is notably lower than the laboratory measurement for that fuel type (Dhammapala et al., 2007b) for an unknown reason.

PCDD/PCDF values were determined from the field aerostat and OBTF samples (ground and airplane samples were not collected due to equipment limitations). Despite creating a multi-burn composite emission sample for each of the biomass types, copious non-detects (NDs) resulted amongst the 17 toxic equivalency factor (TEF)-weighted PCDD/PCDF congeners for the wheat and KBG samples, indicating both low PCDD/PCDF concentrations and that insufficient sample volume was collected to avoid non-detects. In addition, three of the samples had a residual octadibenzofuran (OCDF) congener left over from a previous program's samples that had unexpectedly high concentrations. This affected values for the two HpCDF congeners and the OCDF congener. PCDD/PCDF emission factors are reported in Table 5 with non-detect and contaminated congeners as zeros. Wheat EFs are higher than those for KBG in the field and OBTF. While this difference may be due to the chem-fallow treatment that used salts of 2,4-dichlorophenoxyacetic acid, the limited number of trials makes conclusions premature. In both crop cases, PCDD/PCDF EFs are lower in the OBTF, consistent with observations for  $PM_{25}$ ,  $CH_4$ , and CO. The higher field MCE value for wheat would have been expected to result in lower PCDD/PCDF values, as PCDD/PCDF formation results in part from incomplete carbon combustion(Stieglitz et al., 1989). This observation is limited by the small number of observations for each condition. Congenerspecific data are included in Table S1.

To analyze the potential effect of the non-detect congeners, a second method was used to determine the EF. Seven congeners that were detectable in all six samples were summed and used in a ratio with the one sample that had all 17 congeners detectable. The ratio of the sum of the 7 to 17 congeners for the latter sample was applied to the other samples to calculate the 17-congener, TEF-weighted values for PCDD/PCDF concentration. Results (last row of Table 5) indicate that field-sampled PCDD/PCDF values were about 7–9 times higher than those values from the OBTF, again likely indicative of the higher MCE values observed in the laboratory OBTF burns. Field emission factors for KBG and all wheat were 0.182 and 0.322 ng TEQ/kg burned, respectively, while OBTF values were 0.022 and 0.053 ng TEQ/kg burned. The largest difference between these two methods of PCDD/PCDF EF determinations were found in the OBTF wheat sample (0.144 ng TEQ/kg in the ND = 0 method and 0.053 ng TEQ/kg in the estimated method).

These field PCDD/PCDF results (0.182 and 0.322 ng TEQ/kg) were below previous OBTF emission factor results for wheat stalk burns (0.35–0.60 ng TEQ/kg; (Gullett and Touati, 2003);) and grass burns (0.26–0.56 ng TEQ/kg; (Black et al., 2011);). The same-biomass, laboratory OBTF tests have much lower emission factors than the field tests, differences consistent with results (e.g.,  $PM_{2.5}$ , eBC) cited above. These differences are likely reflective of the higher MCE values in the OBTF. Improved combustion, potentially due to lower moisture levels, higher laboratory ventilation rates, and the absence of the ground heat sink, may be the cause of lower PCDD/PCDF formation.

#### 3.5. Volatile gases and MCE

Emission factors for major and trace volatile gases are shown in Table 6. "Major" gases are defined here as those that are approximately 1% by mass of the total reported VOCs and are reported in order of declining mass. These data are derived from SUMMA canister analyses and reflect a canister fill time of approximately 2 min, ranging from about 30 s to 4 min. Since the canister data included CO measurements, MCE values could be determined, allowing for a robust analysis of the relationship between emission factors and MCE values. Once canister per burn for each of the aerostat, ground, and OBTF was sampled.

Ground-, aerostat-, and OBTF- measured VOC emission factors (Tables S2 and S3) were regressed against MCE using four groupings of data (all sources, field-only, wheat, and KBG) to check for effects of fuel type and for consistency between the field and OBTF measurements. The best fit parameters (slopes and intercepts) of VOC emission factors and MCE regression fits for all data and the field-only data were not statistically different (the standard uncertainty ranges overlapped) for any VOC except propene. For compounds with a minimum of six measurements per fuel type, we evaluated the data for an effect of fuel type on the VOC – MCE relationships by applying Chow's test for heterogeneity of two regressions (Chow, 1960). Statistics for EF-MCE regressions for all VOCs are shown in Table S4. Results for 13 compounds are consistent with a significant fuel type effect (90% confidence level or better) with larger slopes for KBG. Fig. 3 shows emission factor vs. MCE plots for four of these compounds. The regressions predict KBG VOC emission factors to be greater than wheat emission factors by more than 40% at the field average MCE of 0.95. In the case of propene ( $C_3H_6$ ) and naphthalene, there was not a significant relationship between the emission factor and MCE for the wheat, despite robust EF-- MCE relationships for KBG, indicating a fuel type effect for these compounds as well. Six compounds showed strong relationships with MCE that were not significantly affected by fuel type. Nine compounds were not evaluated for fuel type effect due to an insufficient number of measurements.

Nephelometer and CRDS measurements from the airplane for a typical smoke sample are shown in Fig. S3. Each 2 s data point represents a flight segment of approximately 120 m in length based on the typical ground speed of 60 m s<sup>-1</sup> during smoke sampling. The number of data points per smoke sample varied with dispersion conditions. On seven of the eight fires studied, the Cessna airplane sampled emissions over the lifecycle of the fires obtaining multiple samples that transected the plume immediately downwind of the fields. The number of samples depended on the fire size, duration, and dispersion conditions. Thirty five

samples were taken during 8 burns with median altitudes ranging from 850 m to 1450 m. The spatially and temporally extensive plume sampling from the airplane resulted in an estimate of each fire's average MCE and CO<sub>2</sub>, CO, and CH<sub>4</sub> emission factors (Table S5). The average MCE for the wheat burns (0.963) was higher than that for the KBG burns (0.937) (Fig. S4) although no correlation was found between sample height and MCE (r = -0.07, p = 0.67). The MCE difference likely results in part from differences in residue moisture content (RMC), which averaged 31% and 10% for the KBG and wheat fields, respectively. Overall the fire-average MCE decreased with increasing residue moisture content (r = -0.62), although the trend was not statistically significant (p = 0.13), meaning other factors (e.g., time of day, humidity, etc.) contributed to this difference to some degree. The variability in fire-average CH<sub>4</sub> is explained largely by MCE (Fig. 5) such that the CH<sub>4</sub> vs. MCE regression fit is not statistically different from that for the aerostat, ground, and OBTF samples.

The consistent response to MCE suggests the EFVOC - MCE regressions derived from the batch measurements (Table S5) may be used to estimate fire-average emission factors over a range of MCE conditions. Using the EF – MCE regression fits in Table S4, we estimate VOC emission factors (at MCE = 0.957) for direct comparison with the wheat residue emission factors of (Stockwell et al., 2015). The Stockwell et al. (2015) emission factors in Fig. 4 are averages from their laboratory burns (their Table S2, average MCE = 0.957). Comparing the wheat emission factors, with the exception of acetonitrile the emission factors for their study are higher with ratios being 1.4 to 1.8. We may also compare our emission factors for acetonitrile, benzene, and toluene with emission factors measured for agricultural fires in the southeastern U.S. From an airplane platform, Liu et al. (2016) measured emissions from 15 agricultural fires believed to be rice straw. The average MCE of these fires was  $0.93 \pm 0.018$  and average emission factors (mg/kg) were  $169 \pm 123$  for acetonitrile,  $275 \pm 139$  for benzene, and  $167 \pm 91$  for toluene. Using our EF-- MCE relationships from Table S4, we estimate an emission factor (mg/kg) of 173 for acetonitrile, 190 for benzene, and 128 for toluene at MCE = 0.93, which are in reasonable agreement with Liu et al. Finally, CO emission factors are similar to other studies of KBG and wheat crop residue, especially when comparing emission factor measurements made at similar MCE (Dhammapala et al., 2006, Dhammapala et al., 2007a).

# 4. Comparison with field studies of crop residues in the pacific northwest

#### 4.1. Wheat residue

We compared the average of our wheat burn results obtained from the airplane platform (Table S5) with the spring season averages reported previously in eastern Washington (Air Sciences Inc, 2003) with biomass with similar residual moisture content (~10%). There is excellent agreement between the studies with MCE and emissions factors for CO, CH<sub>4</sub>, and PM<sub>2.5</sub>, each differing by < 10%. The ID and WA Chem fallow wheat fields appeared alike and homogeneous resulting in similar PM<sub>2.5</sub> emission factors. Additionally, as shown in Fig. 5, the full spring and fall CH<sub>4</sub> data have a strong linear dependence on MCE (CH<sub>4</sub> =  $-39.3 \pm 3.9 \times MCE + 39.0 \pm 3.7$ , uncertainty of one standard error, R<sup>2</sup> = 0.82) with a slope that is consistent with those observed in our study (i.e., the standard uncertainty ranges overlap).

The consistency between the datasets suggests our VOC – MCE regressions may be generally applicable to the burning of cereal-crop residues. Also plotted in Fig. 5 are CH<sub>4</sub> for the burning of wheat residue as measured in recent laboratory experiments (Stockwell et al., 2014a). The slope of the CH<sub>4</sub> – MCE regression of the (Stockwell et al., 2014a) data is a significant percentage higher than the slope of the CH<sub>4</sub> – MCE regression observed in our study (25% vs. airplane and 70% vs. ground/aerostat/OBTF) or that of the Air Sciences Inc (2003) study (43%). We do not have an explanation for this difference. The limited variation in wheat stubble residue loading (5%) did not result in any observable trends for both PM<sub>2.5</sub> emission factors and MCE.

# 4.2. Kentucky bluegrass

Previous KBG research efforts (Johnston and Golob, 2004) measured emission factors from the burning of KBG in low residue (fields baled post-harvest, ~4.1 tonnes/ha or 1.8 ton/acre) and high residue (~9 tonnes/ha or 4 ton/acre) fields in northern Idaho and eastern Washington to evaluate the effect of pre-burn residue loading on emissions. The focus was PM2.5 emissions, and their study found PM2.5 did not respond significantly to pre-burn residue loading, residue consumption, or residue moisture content. In our work, however, our limited data for both aerostat-, ground-, and airplane-based measurements found that the  $PM_{2.5}$  emission factor was proportional to the dry residue loading (see Fig. 6). A three-fold increase in residue amount appears to be directly associated with higher PM2.5 emissions. This may be due to more smoldering, however, this did not show up in a relationship with MCE. Our limited data (n = 9) show no apparent trend between MCE and residue amounts. This is in contrast to Johnston and Golob (2004) where the average PM2.5 emission factors were roughly the same for the low and high residue burns (28.5 g/kg and 28.2 g/kg, respectively), yet their MCE, CO, and CH<sub>4</sub> were significantly different. For both low and high density fields, CO,  $CH_4$ , and  $PM_{25}$  were much higher than the values measured for the KBG fields burned in our study. Their average emissions for the high residue fields (MCE = 0.82, CO = 211 g/kg, CH<sub>4</sub> = 20.1 g/kg) were consistent with smoldering dominated combustion (Burling et al., 2010, Yokelson et al., 1996). The low residue fields, which had a pre-burn loading similar to the fields in our study, also had emissions consistent with significant smoldering combustion (MCE = 0.87, CO = 147 g/kg, CH<sub>4</sub> = 8.9 g/kg). Johnston and Golob (2004) found that CO and CH<sub>4</sub> increased (and MCE decreased) with increasing residue moisture in the baled fields. However, the large difference in emissions between our study and theirs is not explained by residual moisture content as the KBG fields burned in our study had a higher moisture content (mean = 32% vs. mean = 16% (range 9%-29%)). The CH<sub>4</sub> difference is not explained solely by differences in MCE as our CH<sub>4</sub> – MCE regression curve predicts 5.0 g/kg at MCE = 0.87. The slope of the CH<sub>4</sub> - MCE relationship derived from the Johnston and Golob (2004) data (CH<sub>4</sub> =  $-160 \times MCE + 151$ , R<sup>2</sup> = 0.92) is much higher than the slope of the  $CH_4$  - MCE relationship measured in our study or that of Stockwell et al. (2015), indicating that our VOC - MCE regressions are not consistent with the Johnston and Golob (2004) burns and may not be broadly applicable to the burning of KBG residue. The MCE and emission factors reported by Johnston and Golob (2004) are indicative of fires with significant smoldering combustion and are in stark contrast with MCE and emission factors in our study and Air Sciences Inc (2003). Johnston and Golob (2004) attributed these differences in combustion efficiency in part to changes in the

structure of the fuel (e.g., moist residue on the ground below a drier layer), which was impacted by field management practices. This difference along with the differences observed between the field and OBTF measurements seen here point to the importance of both moisture content and structure of the fuel as important parameters determining the MCE and thus emission factors.

# 5. Conclusions

This work reported and compared emission factors determined from agricultural field burning of wheat stubble and Kentucky bluegrass using ground-, aerostat-, airplane-, and laboratory-based methods of sampling. The biomass density and field treatments varied, resulting in emission factors that represented a range of likely field conditions. Wheat fields burned with a higher MCE than Kentucky bluegrass and resulted in lower emission factors for PM<sub>2.5</sub>, OC, PAHs, CH<sub>4</sub> and CO and higher emission factors for CO<sub>2</sub>, PCDDs/PCDFs, and eBC, as expected. PM<sub>2.5</sub> emission factors for Kentucky bluegrass fields are proportional to residual loading; no such relationship could be observed in the data for wheat stubble fields. Laboratory emission factors differed from those in the field likely due to higher combustion efficiencies in the laboratory as reflected by higher MCE values. This difference may have been due to higher moisture in the field-burned biomass, either in the biomass itself or the soil. Distinctions were observed in some field emission factors that may depend on the sampling platform, however, the minimal overlap of like-instruments and the limited number of replicates limit any definitive statements.

Field and laboratory measurements support the concept of a robust relationship between emission factor values and MCE values that may be used to estimate emissions for wheat and Kentucky bluegrass residues over a wide range of combustion conditions. This robust relationship was demonstrably true for VOCs, where we reported field-measured emission factors for 45 VOCs. To our knowledge, these are the first published wheat and Kentucky bluegrass field-measured emission factors for most of these compounds.

PCDD/PCDF emission factors were consistent with previous biomass combustion results in both laboratory and field sampling. We believe the aerostat-based measurements are the first such aerial emission factors made on agricultural fires.

Very few measurements of aerosol optical properties of fresh emissions from wildland fires are available for comparison, and to our knowledge, there are no published measurements of aerosol absorption for emissions from in-field burning of Kentucky bluegrass or wheat residues. Our published values of Angstrom exponent ( $\alpha$ ) and single scattering albedo ( $\omega$ ) show large differences between field and laboratory measurements, likely due to MCE differences consistent with the emission factor determinations. Greater combustion efficiency (higher MCE) is associated with lower  $\alpha$  and  $\omega$  values.

For the fires sampled in this study, the agricultural residue types burned with different fireaverage MCE: 0.963 for wheat and 0.937 for Kentucky bluegrass. However, the extent to which the combustion conditions (MCE) of these fires represent burning throughout the Pacific Northwest is uncertain. The wheat residue burned in this study was dry (RMC <

15%) and fire-average MCE =  $0.963 (\pm 0.011)$ , suggesting that our emission factors are applicable across the Pacific Northwest for dry wheat residue.

# Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

# Acknowledgments

This project was made possible by a Regional Applied Research Effort grant from EPA's Office of Research and Development in conjunction with EPA Region 10 and contributions from the U.S. Forest Service. The Idaho Department of Environmental Quality, the Nez Perce Tribe Air Quality Program, the National Oceanographic and Atmospheric Administration (NOAA)/National Weather Service (Spokane office), and the Washington Department of Ecology are expressly thanked for their hospitality and cooperation in conducting the burns. We thank the US Forest Service Northern Rockies Fire and Aviation for supporting this research with special thanks to our pilot Tony Sleznick and Regional Aviation Officer Maggie Doherty. We also thank Spus Wilder and Conamara Burke (Colorado State University) for leading the fuels collection effort and Bakul Patel (Senior Environmental Employment program) for the EC/OC analyses. Finally, we appreciate the cooperation of the farmers and burners who participated in our study.

# References

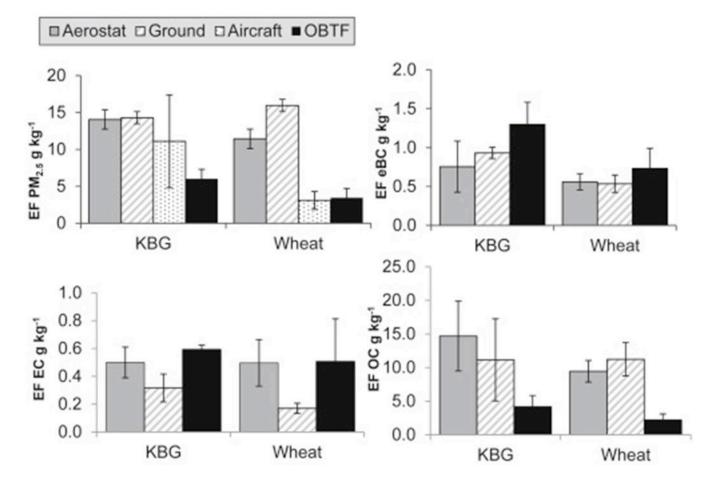
- Air Sciences Inc, 2003 Air Sciences Inc Cereal-grain Residue Open-field Burning Emissions Study (2003) http://www.ecy.wa.gov/programs/air/pdfs/FinalWheat\_081303.pdf
- Abel et al., 2003 Abel SJ, Haywood JM, Highwood EJ, Li J, Buseck PR Evolution of biomass burning aerosol properties from an agricultural fire in southern Africa Geophys. Res. Lett, 30 (2003)
- Aurell and Gullett, 2010 Aurell J, Gullett BK Aerostat sampling of PCDD/PCDF emissions from the Gulf oil spill in situ burns Environ. Sci. Technol, 44 (2010), pp. 9431–9437 [PubMed: 21073185]
- Aurell and Gullett, 2013 Aurell J, Gullett BK Emission factors from aerial and ground measurements of field and laboratory forest burns in the southeastern US: PM2. 5, black and brown carbon, VOC, and PCDD/PCDF Environ. Sci. Technol, 47 (2013), pp. 8443–8452 [PubMed: 23895511]
- Aurell et al., 2012 Aurell J, Gullett BK, Yamamoto D Emissions from open burning of simulated military waste from forward operating bases Environ. Sci. Technol, 46 (2012), pp. 11004–11012 [PubMed: 22992062]
- Aurell et al., 2015 Aurell J, Gullett BK, Tabor D Emissions from southeastern US Grasslands and pine savannas: comparison of aerial and ground field measurements with laboratory burns Atmos. Environ, 111 (2015), pp. 170–178
- Baker et al., 2016 Baker K, Woody M, Tonnesen G, Hutzell W, Pye H, Beaver M, Pouliot G, Pierce T Contribution of regional-scale fire events to ozone and PM 2.5 air quality estimated by photochemical modeling approaches Atmos. Environ, 140 (2016), pp. 539–554
- Black et al., 2011 Black RR, Meyer CP, Touati A, Gullett BK, Fiedler H, Mueller JF Emissions of PCDD and PCDF from combustion of forest fuels and sugarcane: a comparison between field measurements and simulations in a laboratory burn facility Chemosphere, 83 (2011), pp. 1331–1338 [PubMed: 21524778]
- Burling et al., 2010 Burling IR, Yokelson RJ, Griffith DWT, Johnson TJ, Veres P, Roberts JM, Warneke C, Urbanski SP, Reardon J, Weise DR, et al., Laboratory measurements of trace gas emissions from biomass burning of fuel types from the southeastern and southwestern United States Atmos. Chem. Phys, 10 (2010), pp. 11115–11130
- CFR, 1987 40 Code of Federal Regulations, Appendix L Reference Method for the Determination of Particulate Matter as PM2.5 in the Atmosphere (1987)
- Chow, 1960 Chow GC Tests of equality between sets of coefficients in two linear regression Econometrica, 28 (1960), pp. 591–605
- Dhammapala et al., 2006 Dhammapala R, Claiborn C, Corkill J, Gullett B Particulate emissions from wheat and Kentucky bluegrass stubble burning in eastern Washington and northern Idaho Atmos. Environ, 40 (2006), pp. 1007–1015

- Dhammapala et al., 2007a Dhammapala R, Claiborn C, Jimenez J, Corkill J, Gullett B, Simpson C, Paulsen MEmission factors of PAHs, methoxyphenols, levoglucosan, elemental carbon and organic carbon from simulated wheat and Kentucky bluegrass stubble burns Atmos. Environ, 41 (2007), pp. 2660–2669
- Dhammapala et al., 2007b Dhammapala R, Clasiborn C, Simpson C, Jimenez J Emission factors from wheat and Kentucky bluegrass stubble burning: comparison of field and simulated burn experiments Atmos. Environ, 41 (2007), pp. 1512–1520
- Grandesso et al., 2011 Grandesso E, Gullett B, Touati A, Tabor D Effect of moisture, charge size, and chlorine concentration on PCDD/F emissions from simulated open burning of forest biomass Environ. Sci. Technol, 45 (2011), pp. 3887–3894 [PubMed: 21469704]
- Gullett and Touati, 2003 Gullett B, Touati A PCDD/F emissions from burning wheat and rice field residue Atmos. Environ, 37 (2003), pp. 4893–4899
- Hagler et al., 2011 Hagler GS, Yelverton TL, Vedantham R, Hansen AD, Turner JR Post-processing method to reduce noise while preserving high time resolution in aethalometer real-time black carbon data Aerosol Air Qual. Res, 11 (2011), pp. 539–546
- Hart et al., 2012 Hart JM, Anderson NP, Hulting AG, Chastain TG, Mellbye ME, Young WC III, Silberstein TB Postharvest Residue Management for Grass Seed Production in Western Oregon (2012) https://catalog.extension.oregonstate.edu/em9051
- Holder et al., 2016 Holder AL, Hagler GS, Aurell J, Hays MD, Gullett BK Particulate matter and black carbon optical properties and emission factors from prescribed fires in the southeastern United States J. Geophys. Res. Atmos, 121 (2016), pp. 3465–3483
- Huggins, 2005 Huggins D Straw Management and Crop Rotation Alternatives to Stubble Burning: Final Report (2005) http://www.ecy.wa.gov/programs/air/aginfo/research\_pdf\_files/ DOE\_Final\_Report\_CropRotation.pdf
- Jain et al., 2007 Jain R, Vaughan J, Heitkamp K, Ramos C, Claiborn C, Schreuder M, Schaaf M, Lamb B Development of the ClearSky smoke dispersion forecast system for agricultural field burning in the Pacific Northwest Atmos. Environ, 41 (2007), pp. 6745–6761
- Johnston and Golob, 2004 Johnston W, Golob C Quantifying Post-harvest Emissions from Bluegrass Seed Production Field Burning Department of Crop and Soil Sciences, Washington State University, Pullman, WA (2004)
- Khan et al., 2012 Khan B, Hays MD, Geron C, Jetter J Differences in the OC/EC ratios that characterize ambient and source aerosols due to thermal-optical analysis Aerosol Sci. Technol, 46 (2012), pp. 127–137
- Kondo et al., 2011 Kondo Y, Matsui H, Moteki N, Sahu L, Takegawa N, Kajino M, Zhao Y, Cubison M, Jimenez J, Vay S Emissions of black carbon, organic, and inorganic aerosols from biomass burning in North America and Asia in 2008 J. Geophys. Res. Atmos, 116 (2011)
- Kumar and Goh, 1999 Kumar K, Goh K Crop residues and management practices: effects on soil quality, soil nitrogen dynamics, crop yield, and nitrogen recovery Adv. Agron, 68 (1999), pp. 197– 319
- Larsen and Larsen, 1998 Larsen JC, Larsen PB Chemical carcinogens Issues Environ. Sci. Technol, 10 (1998), pp. 33–56
- Laskin et al., 2015 Laskin A, Laskin J, Nizkorodov SA Chemistry of atmospheric brown carbon Chem. Rev, 115 (2015), pp. 4335–4382 [PubMed: 25716026]
- Lewis et al., 2008 Lewis K, Arnott WP, Moosmüller H, Wold CE Strong spectral variation of biomass smoke light absorption and single scattering albedo observed with a novel dual-wavelength photoacoustic instrument J. Geophys. Res. Atmos, 113 (2008)
- Liu et al., 2014 Liu S, Aiken AC, Arata C, Dubey MK, Stockwell CE, Yokelson RJ, Stone EA, Jayarathne T, Robinson AL, DeMott PJ Aerosol single scattering albedo dependence on biomass combustion efficiency: laboratory and field studies Geophys. Res. Lett, 41 (2014), pp. 742–748
- Liu et al., 2016 Liu X, Zhang Y, Huey L, Yokelson R, Wang Y, Jimenez J, Campuzano-Jost P, Beyersdorf A, Blake D, Choi Y Agricultural fires in the southeastern US during SEAC4RS: emissions of trace gases and particles and evolution of ozone, reactive nitrogen, and organic aerosol J. Geophys. Res. Atmos, 121 (12) (2016), pp. 7383–7414

- May et al., 2014 May A, McMeeking G, Lee T, Taylor J, Craven J, Burling I, Sullivan A, Akagi S, Collett J, Flynn M Aerosol emissions from prescribed fires in the United States: a synthesis of laboratory and aircraft measurements J. Geophys. Res. Atmos, 119 (2014)
- McCarty, 2011 McCarty JL Remote sensing-based estimates of annual and seasonal emissions from crop residue burning in the contiguous United States J. Air & Waste Manag. Assoc, 61 (2011), pp. 22–34 [PubMed: 21305885]
- McCarty et al., 2009 McCarty JL, Korontzi S, Justice CO, Loboda T The spatial and temporal distribution of crop residue burning in the contiguous United States Sci. Total Environ, 407 (2009), pp. 5701–5712 [PubMed: 19647857]
- McMeeking et al., 2014 McMeeking G, Fortner E, Onasch T, Taylor J, Flynn M, Coe H, Kreidenweis S Impacts of nonrefractory material on light absorption by aerosols emitted from biomass burning J. Geophys. Res. Atmos, 119 (2014)
- National Institute for Occupational Safety and Health, 2016 National Institute for Occupational Safety and Health NIOSH Manual of Analytical Methods (NMAM) (fifth ed.) (2016) https:// www.cdc.gov/niosh/nmam/default.html
- Petzold et al., 2013 Petzold A, Ogren JA, Fiebig M, Laj P, Li S-M, Baltensperger UHolzer-Popp T, Kinne S, Pappalardo G, Sugimoto N Recommendations for reporting" black carbon" measurements Atmos. Chem. Phys, 13 (2013), pp. 8365–8379
- Pouliot et al., 2016 Pouliot G, Rao V, McCarty JL, Soja A Development of the crop residue and rangeland burning in the 2014 National emissions inventory using information from multiple sources J. Air Waste Manag., Null-Null, 67 (5) (2016), pp. 613–622
- Reid and Hobbs, 1998 Reid JS, Hobbs PV Physical and optical properties of young smoke from individual biomass fires in Brazil J. Geophys. Res. Atmos, 103 (1998), pp. 32013–32030
- SAFE AIR FOR EVERYONE v. MEYER, 2004 SAFE AIR FOR EVERYONE v. MEYER 2004 373 F.3d 1035. United States Court of Appeals, Ninth Circuit. http://openjurist.org/373/f3d/1035/safeair-for-everyone-v-meyer.
- SAFE AIR FOR EVERYONE v. U.S. EPA, 2007 SAFE AIR FOR EVERYONE v. U.S. EPA 2007 475 F.3d 1096, 1102 (9th Cir. 2007). https://casetext.com/case/safe-air-for-everyone-v-us-epa.
- Sahu et al., 2012 Sahu L, Kondo Y, Moteki N, Takegawa N, Zhao Y, Cubison M, Jimenez J, Vay S, Diskin G, Wisthaler A Emission characteristics of black carbon in anthropogenic and biomass burning plumes over California during ARCTAS-CARB 2008 J. Geophys. Res. Atmos, 117 (2012)
- Schwarz et al., 2008 Schwarz J, Gao R, Spackman J, Watts L, Thomson D, Fahey D, Ryerson T, Peischl J, Holloway J, Trainer M Measurement of the mixing state, mass, and optical size of individual black carbon particles in urban and biomass burning emissions Geophys. Res. Lett, 35 (2008)
- Seattlepi, 2003 Seattlepi Field Burning Fills the Air with Smoke (2003) http://www.seattlepi.com/ news/article/Field-burning-fills-the-air-with-smoke-1121435.php
- Spokesman-Review, 2005 Spokesman-Review Field-burning Lawsuit Settles for \$891,450 (2005) http://www.spokesman.com/stories/2005/nov/15/field-burning-lawsuit-settles-for-891450/
- Stieglitz et al., 1989 Stieglitz L, Zwick G, Beck J, Bautz H, Roth W Carbonaceous particles in fly ash – a source for the de novo synthesis of organochlorocompounds Chemosphere, 19 (1989), pp. 283–290
- Stockwell et al., 2014a Stockwell C, Yokelson R, Kreidenweis S, Robinson A, DeMott P, Sullivan R, Reardon J, Ryan K, Griffith D, Stevens L Trace gas emissions from combustion of peat, crop residue, biofuels, grasses, and other fuels: configuration and FTIR component of the fourth Fire Lab at Missoula Experiment (FLAME-4) Atmos. Chem. Phys. Discuss, 14 (2014)
- Stockwell et al., 2014b Stockwell CE, Yokelson RJ, Kreidenweis SM, Robinson AL, DeMott PJ, Sullivan RC, Reardon J, Ryan KC, Griffith DWT, Stevens Trace gas emissions from combustion of peat, crop residue, domestic biofuels, grasses, and other fuels: configuration and Fourier transform infrared (FTIR) component of the fourth Fire Lab at Missoula Experiment (FLAME-4) Atmos. Chem. Phys, 14 (2014), pp. 9727–9754
- Stockwell et al., 2015 Stockwell C, Veres P, Williams J, Yokelson R Characterization of biomass burning emissions from cooking fires, peat, crop residue, and other fuels with high-resolution

proton-transfer-reaction time-of-flight mass spectrometry Atmos. Chem. Phys, 15 (2015), pp. 845-865

- Subramanian et al., 2004 Subramanian R, Khlystov AY, Cabada JC, Robinson AL Positive and negative artifacts in particulate organic carbon measurements with denuded and undenuded sampler configurations special issue of aerosol science and Technology on findings from the fine particulate matter supersites program Aerosol Sci. Technol, 38 (2004), pp. 27-48
- U.S. Department of Agriculture Crop Production 2014 Summary (2015) ISSN: 1057-7823. U.S. Department of Agriculture, 2015https://www.census.gov/history/pdf/cropan15.pdf
- Urbanski, 2013 Urbanski S Combustion efficiency and emission factors for wildfire-season fires in mixed conifer forests of the northern Rocky Mountains US. Atmos. Chem. Phys, 13 (2013), pp. 7241-7262
- U.S. EPA, 1999a U.S. EPA Compendium Method TO-9A, Determination of Polychlorinated, Polybrominated and Brominated/Chlorinated Dibenzo-p-dioxins and Dibenzofurans in Ambient Air (1999)
- U.S. EPA, 1999b U.S. EPA Compendium Method TO-15, Determination of Volatile Organic Compounds (VOCs) in Air Collected in Specially-prepared Canisters and Analyzed by Gas Chromatography/mass Spectrometry (GC/MS) (1999)
- U.S. EPA Method 25C, 2016 U.S. EPA, 2016 Method 25C, Determination of nonmethane organic compounds (NMOC) in landfill gases.
- U.S. EPA, 1989 U.S. EPA Method 3A, Determination of Oxygen and Carbon Dioxide Concentrations in Emissions from Stationary Sources (Instrumental Analyzer Procedure) (1989)
- Van den Berg et al., 2006 Van den Berg M, Birnbaum LS, Denison M, De Vito M, Farland W, Feeley M, Fiedler H, Hakansson H, Hanberg A, Haws L The 2005 World Health Organization reevaluation of human and mammalian toxic equivalency factors for dioxins and dioxin-like compounds Toxicol. Sci, 93 (2006), pp. 223-241 [PubMed: 16829543]
- Vaughan et al., 2004 Vaughan J, Lamb B, Frei C, Wilson R A numerical daily air quality forecast system for the Pacific Northwest Bull. Am. Meteorol. Soc, 85 (2004), p. 549
- Ward et al., 1979 Ward DE, Nelson RM, and Adams DF 1979 Forest fire smoke plume documentation. Proceedings of the Seventy-Seventh Annual Meeting of the Air Pollution Control Association Pap. 079-6.3.
- Winijkul et al., 2015 Winijkul E, Yan F, Lu Z, Streets D, Bond T, Zhao Y Size-resolved global emission inventory of primary particulate matter from energy-related combustion sources Atmos. Environ, 107 (2015), pp. 137-147
- Wulfhorst et al., 2006 Wulfhorst J, Van Tassell L, Johnson B, Holman J Thill D An Industry amidst Conflict and Change: Practices and Perceptions of Idaho's Bluegrass Seed Producers: Citeseer) (2006)
- Yokelson et al., 1996 Yokelson RJ, Griffith DWT, Ward DE Open-path Fourier transform infrared studies of large-scale laboratory biomass fires J.Geophys Res-Atmos, 101 (1996), pp. 21067-21080

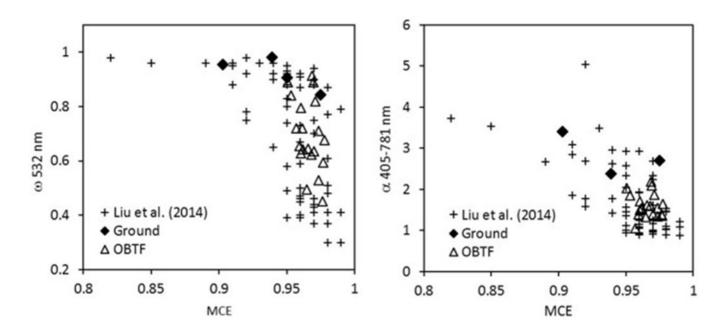


# Fig. 1.

Average  $PM_{2.5}$ , EC, eBC, and OC emission factors. Bars indicate  $\pm 1$  standard deviation (std.).

Holder et al.



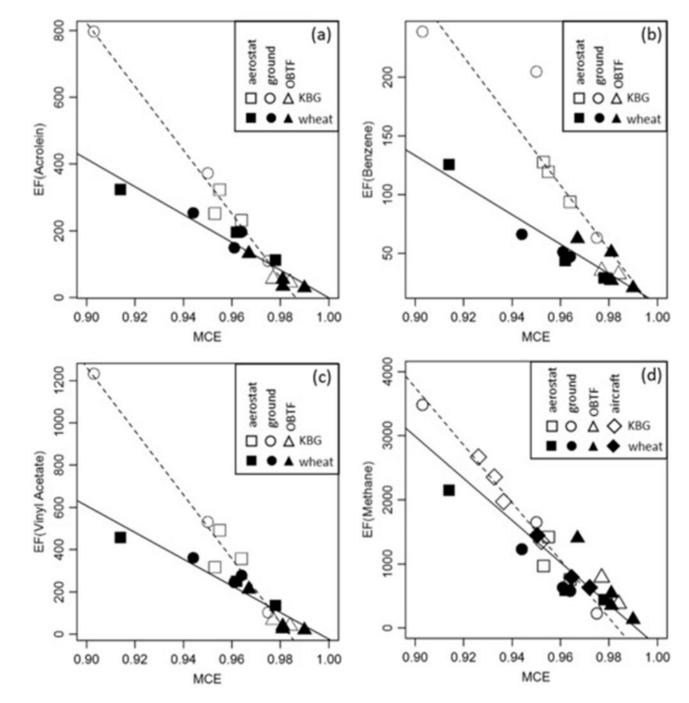


# Fig. 2.

Single scattering albedo ( $\omega$ ) at 532 nm and absorption angstrom exponent ( $\alpha$ ) for 405–781 nm for burn averaged values. "Ground" CO measurements for MCE are 2 min samples and may not be reflective of the whole burn. Liu et al. (2014) measurements are for wheat and a variety of grass species.

Holder et al.

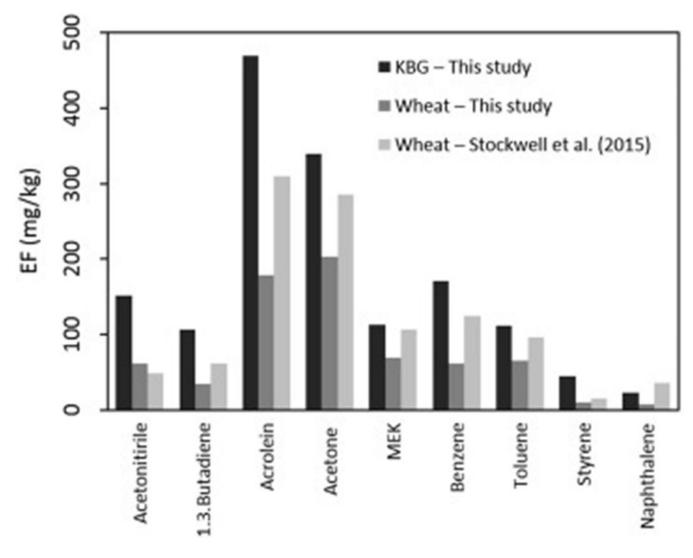
Page 21



# Fig. 3.

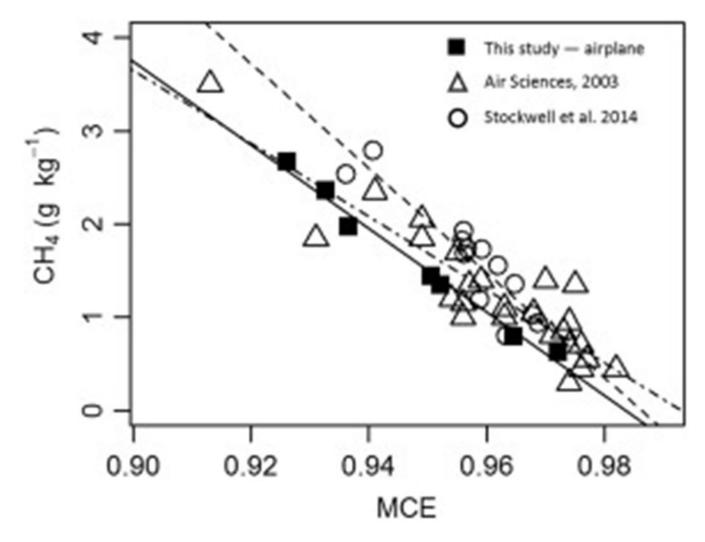
Select VOC emission factors (mg/kg) as a function of MCE (a–c) for the ground, aerostat, and OBTF platforms where the solid and dashed lines are linear regression best fit for wheat and KBG, respectively, and (d) for the ground, aerostat, OBTF, and airplane platforms where the solid and dashed lines are linear regression best fit for ground, aerostat, and OBTF (solid) and airplane (dashed) platforms.

Holder et al.





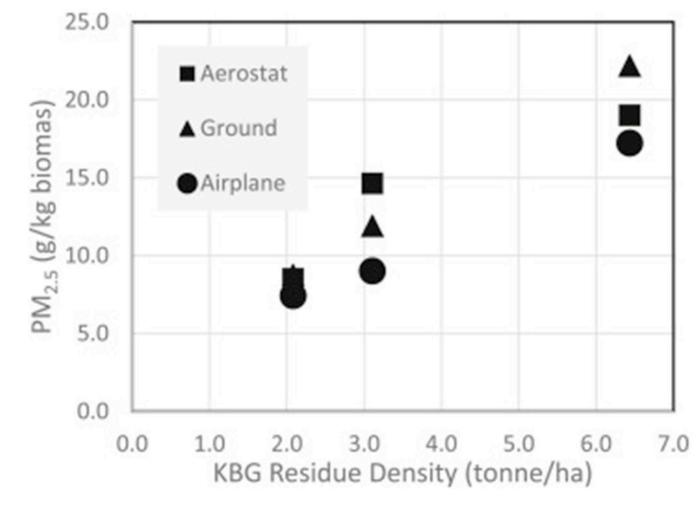
Comparison of VOC emission factors between estimates made here for the combined ground, aerostat, and OBTF platforms with Stockwell et al., 2015. Emission factors shown for our study have been adjusted to the MCE of the Stockwell et al. study (0.957).



# Fig. 5.

Methane (CH<sub>4</sub>) emission factors as a function of MCE for fire average values measured in this study from the airplane platform (Solid line, slope =  $-44.9 (\pm 2.5)$ , R<sup>2</sup> = 0.98) and from literature (dashed line, slope =  $-56.2 (\pm 7.5)$ , R<sup>2</sup> = 0.84 (Stockwell et al., 2014b), and dash-dot line, slope =  $-39.3 (\pm 3.9)$ , R<sup>2</sup> = 0.81, Air Sciences Inc (2003).

Holder et al.



# Fig. 6.

Effect of KBG crop residue density (dry weight) on PM2.5 emission factors across all platforms. PM from field B and LL were gathered on the same sample media.

# Table 1.

Burn location, and fuel information.

Burn No.	Location	Field ID	Fuel Type	Fuel Load (kg m <sup>-2</sup> )	Stubble Height (m)	Moisture Content (%)	Size (ha)
1	Nez Perce, ID	KBG B	Kentucky Bluegrass baled, light fuel load	0.26	0.13	32	66
2	Nez Perce, ID	KBG LL	Kentucky Bluegrass light fuel load	0.36	0.14	31	66
3	Nez Perce, ID	Wheat	Wheat post-harvest stubble	0.37	0.18	11	66
4	Nez Perce, ID	KBG HL	Kentucky Bluegrass high fuel load	0.64	0.10	21	66
5	Nez Perce, ID	KBG B2	Kentucky Bluegrass baled	NS	NS	42	66
6	Walla Walla, WA	Wheat CF1	Wheat - Chem-fallow	0.69	0.38	11	96
7 <sup><i>a</i></sup>	Walla Walla, WA	Wheat CF2	Wheat - Chem-fallow	NS	NS	7	36
8	Walla Walla, WA	Wheat CF3	Wheat - Chem-fallow	0.76	0.42	8	27

<sup>a</sup>All platforms except airplane.

# Table 2.

# Analytes, instrumentation, and methods.

Analytes	Instrument	Mode	Sampling period/rate	Analyses and methods		
Ground and aerostat meas	surements					
Equivalent Black carbon (eBC)	AE51 <sup>a</sup>	Continuous	every second	Filter attenuation at 880 nm		
PM <sub>2.5</sub>	Impactor $^{b}$ , 47 mm Teflon filter		10 L/min	Gravimetric, 40 CFR Part 50, Appendix L (1987)		
PCDD/PCDF <sup>C</sup> PAHs <sup>d</sup>	Quartz filter/PUF PUF/XAD	Batch Batch	850 L/min 150 L/min	HRGC/HRMS, modified Method TO-9A (1999a)		
VOCs	SUMMA Canister	Batch	~2 min	GC/LRMS, Method TO-15 (1999b)		
EC, OC, TC	Impactor, quartz filter	Batch	10 L/min	Thermal/optical, NIOSH 5040 (2016)		
CO, CO <sub>2</sub> , CH <sub>4</sub>	SUMMA Canister	Batch	~2 min	GC, Method 25C (2016)		
CO <sub>2</sub>	O <sub>2</sub> LICOR-820 <sup>e</sup>		every second	non-dispersive infrared (NDIR), Method 3A (1989)		
Ground aerosol optical me	easurements					
Refractory Black carbon (rBC)	Single Particle Soot Photometer (SP2)	Continuous	every second	Laser induced incandescence		
Absorption and Scattering	Photoacoustic Soot Spectrometer (PASS-3)	Continuous	2 s	Photoacoustic absorption, reciprocal nephelometer		
Airplane: Cessna-206 mea	surements					
$CO, CO_2, CH_4$	$D, CO_2, CH_4$ Picarro G2401-m <sup>f</sup>		2 s, 0.5 L/min	Cavity ring-down spectroscopy		
Inferred PM <sub>2.5</sub>	RR903 nephelometer $^{g}$	Continuous	2 s, 16.7 L/min	Integrated scattering 530 nm		

<sup>a</sup>AethLabs, U.S.

<sup>b</sup>SKC Inc., U.S.

<sup>C</sup>Only aerostat-based samples were taken.

<sup>d</sup>Only ground-based samples were taken.

<sup>e</sup>LiCOR Biosciences, U.S.

f Picarro, Inc., U.S.

<sup>g</sup>Radiance Research, U.S.

.

#### Table 3.

Aerostat, ground, airplane, and OBTF PM2.5-associated emission factors (in g/kg) by fuel type.

Fuel Type	Platform	MCE	PM <sub>2.5</sub>	тс	OC	EC	eBC <sup><i>a</i></sup>
KBG	Aerostat		$14\pm5.3$	$15\pm5.2$	$15\pm5.2$	$0.50\pm0.11$	$0.76\pm0.33$
	Ground		$14\pm7.0$	$11\pm 6.1$	$11\pm 6.1$	$0.32\pm0.10$	$0.93\pm0.073$
	Airplane	0.93	$(11.1\pm6.3)$	NS	NS	NS	NS
	OBTF	0.98	$\begin{array}{c} 6.0 \pm 2.2 \\ (5.8 \pm 2.1) \end{array}$	$\begin{array}{c} 4.8 \pm 1.6 \\ (4.6 \pm 1.6) \end{array}$	$\begin{array}{c} 4.2 \pm 1.7 \\ (4.0 \pm 1.6) \end{array}$	$\begin{array}{c} 0.59 \pm 0.033 \\ (0.57 \pm 0.033) \end{array}$	$\begin{array}{c} 1.3 \pm 0.28 \\ (1.3 \pm 0.26) \end{array}$
Wheat	Aerostat		$11.4 \pm 1.5$	$9.9 \pm 1.5$	$9.4 \pm 1.6$	$0.5\pm0.2$	$0.6\pm0.1$
	Ground		$16.0\pm4.9$	$11.4\pm2.4$	$11.2\pm2.5$	$0.2\pm0.0$	$0.5\pm0.1$
	Airplane	0.96	$(3.1\pm1.2)$	NS	NS	NS	NS
	OBTF	0.98	$\begin{array}{c} 3.5 \pm 1.9 \\ (3.3 \pm 1.8) \end{array}$	$\begin{array}{c} 2.7 \pm 1.3 \\ (3.1 \pm 1.3) \end{array}$	$\begin{array}{c} 2.2 \pm 1.3 \\ (2.1 \pm 1.2) \end{array}$	$\begin{array}{c} 0.51 \pm 0.31 \\ (0.49 \pm 0.29) \end{array}$	$\begin{array}{c} 0.73 \pm 0.26 \\ (0.69 \pm 0.24) \end{array}$

Emission factors calculated with both CO and CO2 as the carbon source are within parentheses. Others are CO2 only.

NS - not sampled.

Uncertainty,  $\pm$ , is one standard deviation.

 $^{a}$ eBC collected during the same time frame as the PM2.5 batch filter.

# Table 4.

Aerosol optical properties and size distribution by fuel type and by platform.

Fuel Type	Platform	MCE <sup>a</sup>	EC/TC	ω	a		$D_m(nm)$	σg
				532 nm	405-781 nm	405-532 nm		
KBG	Ground	$0.94\pm0.037$	$0.038\pm0.013$	$0.90\pm0.05$	$3.1\pm0.42$	$4.00\pm0.59$	$164 \pm 7$	$1.49\pm0.01$
		(3)	(4)	(4)	(2)	(2)	(4)	(4)
	OBTF	$0.96\pm0.004$	$0.139\pm0.064$	$0.67\pm0.07$	$1.60\pm0.08$	$1.48\pm0.30$	$173\pm4$	$1.46\pm0.01$
		(9)	(3)	(5)	(5)	(5)	(5)	(5)
Wheat	Ground	0.94	$0.024\pm0.016$	$0.96\pm0.04$	$2.54\pm0.31$	$3.4\pm0.76$	$165\pm10$	$1.53\pm0.01$
		(1)	(4)	(2)	(2)	(2)	(3)	(3)
	OBTF	$0.97\pm0.009$	$0.190\pm0.091$	$0.70\pm0.15$	$1.60\pm0.33$	$2.27\pm0.61$	$168\pm5$	$1.50\pm0.03$
		(17)	(6)	(15)	(15)	(15)	(17)	(17)

Numbers in parentheses denote number of measurements.

Uncertainty,  $\pm$ , is one standard deviation, or range for two measurements.

<sup>a</sup>MCE calculated from 1 to 2 min sample may not be reflective of the entire burn.

#### Table 5.

# PAH emission factors in mg/kg.

РАН	KBG	Wheat		
	Field <sup><math>a</math></sup> (n = 2)	$OBTF^{b}$ (n = 1)	Field (n = 3)	<b>OBTF</b> (n = 2)
mg/kg biomass				
Naphthalene	$26.51\pm0.24$	7.81	$22.19\pm2.14$	$6.97 \pm 2.15$
Acenaphthylene	$9.02 \pm 1.00$	1.65	$2.40\pm0.54$	$1.73\pm0.54$
Acenaphthene	$1.22\pm0.18$	0.28	$0.53 \pm 0.1$	$0.23\pm0.1$
Fluorene	$3.38 \pm 0.71$	1.25	$2.33 \pm 0.52$	$1.13\pm0.52$
Phenanthrene	$6.30\pm0.46$	1.53	$2.46\pm0.56$	$1.57\pm0.56$
Anthracene	$1.41\pm0.07$	0.52	$0.70\pm0.21$	$0.48 \pm 0.21$
Fluoranthene	$1.82\pm0.39$	0.50	$0.59\pm0.16$	$0.47\pm0.16$
Pyrene	$1.50\pm0.38$	0.45	$0.45\pm0.11$	$0.42\pm0.11$
Benzo(a)anthracene	$0.45\pm0.11$	0.16	$0.16\pm0.05$	$0.17\pm0.05$
Chrysene	$0.57\pm0.04$	0.15	$0.22\pm0.03$	$0.15\pm0.03$
Benzo(b)fluoranthene	$0.28\pm0.05$	0.07	$0.27\pm0.02$	$0.07\pm0.02$
Benzo(k)fluoranthene	$0.39 \pm 0.14$	0.06	$0.46\pm0.01$	$0.07\pm0.01$
Benzo(a)pyrene	$0.27\pm0.10$	0.09	$0.08\pm0.03$	$0.09\pm0.03$
Indeno(1,2,3-cd)pyrene	$0.16\pm0.07$	0.05	$0.04\pm0.02$	$0.05\pm0.02$
Dibenz(a,h)anthracene	$0.04\pm0.00$	0.01	$0.02\pm0$	$0.01\pm0$
Benzo(ghi)perylene	$0.17\pm0.08$	0.04	$0.04\pm0.01$	$0.05\pm0.01$
Sum of reported PAHs	$53.49 \pm 2.25$	14.61	$32.95 \pm 4.51$	$13.65\pm4.51$
Sum as mg B[a]P TEQ/kg biomass	$0.49\pm0.15$	0.15	$0.20\pm0.04$	$0.15\pm0.04$
РАН	Field <sup><math>a</math></sup> (n = 1)	<b>OBTF</b> <sup><math>b</math></sup> (n = 1)	Field <sup><math>a</math></sup> (n = 2)	$OBTF^2$ (n = 2
ng/kg biomass				
PCDD TEQ	0.130	0.003	0.250	0.083
PCDF TEQ	0.052	0.017	0.072	0.061
PCDD, PCDF TEQ	0.182	0.020	0.322	0.144
PCDD, PCDF TEQ -congener ratio method	0.182	0.022	0.362	0.053

 $^{a}\mathrm{EFs}$  based on CO2 measurements only. Ground-based measurements only.

*b* Emission factors from the OBTF that also include CO values (only available from the OBTF) show less than a 5% decline in EF values from those calculated with CO<sub>2</sub> only.

# Table 6.

# Emission factors for major and select trace gases.

Compound	KBG			Wheat						
	Aerostat	Ground	OBTF	AVG	STD	Aerostat	Ground	OBTF	AVG	STD
MCE	0.96 <sup>a</sup>	0.94 <sup><i>a</i></sup>	0.98	0.96	0.02	0.95 <sup>a</sup>	0.96 <sup>a</sup>	0.98	0.96	0.02
	g/kg biomass					g/kg biomass				
Methane	1.0	1.8	0.58	1.1	0.61	1.1	0.81	0.61	0.83	0.23
Carbon Monoxide	44.0	59.	20.	41.	20	47.	42.	20.	37	14.
Carbon Dioxide	1600	1500	1600	1600	33	1500	1500	1500	1500	47.0
Sum of VOCs <sup>b</sup>	1.7	2.3	0.36	1.4	0.97	1.2	1.0	0.61	0.96	0.32
	mg/kg bio	mass				mg/kg bio	mass			
Vinyl Acetate	390	620	53	360	290	280	300	73	220	124
Acrolein	270	430	51	250	190	210	200	62	160	83
Acetone	270	200	ND	240	52	210	150	27	130	94
Propene	190	290	120	200	84	150	110	280	180	87
Benzene	110	170	34	110	68	66	55	40	54	13
Toluene	96	140	32	89	54	120	39	ND	80	58
Acetonitrile	97	130	27	84	51	82	53	12	49	35
2-Butanone (MEK)	82	240	19	110	110	130	42	27	67	56
1,3-Butadiene	68	90	2.2	53	46	42	25	15	27	14
Acrylonitrile	36	46	8.2	30.	20	18	14	3.4	12	7.5
Styrene	28	41	1.9	23	20	13	9.4	4.6	9.0	4.3
m-,p-Xylenes	17	27	5.7	17	11	11	8.7	6.1	8.7	2.6

<sup>a</sup>CO measurements from SUMMA canister grab sample.

<sup>b</sup>Sum of detectable compounds.