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AEROSOL RESEARCH LETTER

Chemical Smoke Marker Emissions During Flaming and Smoldering Phases of Laboratory Open Burning of Wildland Fuels

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[Supplementary materials are available for this article. Go to the publisher's online edition of *Aerosol Science and Technology* to view the free supplementary files.]

1. INTRODUCTION

Smoke emitted by prescribed and wild fires can make a substantial contribution to ambient aerosol (McMeeking et al. 2006; Park et al. 2007; Spracklen et al. 2007). Approaches to investigate these contributions have used a variety of different chemical smoke markers, including levoglucosan, produced by thermal degradation of cellulose, and water-soluble potassium (Andreae 1983; Engling et al. 2006; Hays et al. 2002; Simoneit 2002; Ward et al. 2006). Filter sampling is commonly employed to measure smoke markers in ambient and source samples; however, these time-integrated measurements limit knowledge about variability of smoke marker emissions, especially between flaming and smoldering fire phases.

Recently developed instruments, such as the Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (HR-AMS, AMS hereinafter for short), allow aerosol composition measurements with time resolution of seconds (Canagaratna et al. 2007; DeCarlo et al. 2006). Fragments with mass-to-charge (m/z) ratios of 60.021 ($C_2H_4O_2^+$) and 73.029 ($C_3H_5O_2^+$) have been suggested as AMS biomass burning markers (Alfarra et al. 2007; Mohr et al. 2009; Schneider et al. 2006). Weimer et al. (2008) reported quadrupole AMS observations of primary smoke particles from flaming and smoldering phases of domestic wood burning. In this article, AMS data are used for the first time to examine key smoke markers emitted during the flaming and smoldering phases from open burning of numerous wildland fuel types. Key AMS smoke marker data presented include *m/z* 38.964 and *m/z* 60.021 (referred to as K^+ and $C_2H_4O_2^+$ hereafter). We also compare $C_2H_4O_2^+$ measured by the AMS to concentrations of anhydrosugars (levoglucosan, mannosan, and galactosan) obtained by analyzing filter samples (Sullivan et al. 2008). Such observations are key to understanding what ambient AMS marker measurements reveal about primary particle contributions from biomass burning.

2. INSTRUMENTATION

During the second Fire Lab at Missoula Experiment (FLAME II), small quantities (~250 g) of more than 20 different biomass fuel types were combusted in an "open burning" configuration. More information on the combustion facility, fuels used, types of burns conducted, and chemical analysis of collected filter samples can be found in Sullivan et al. (2008) and McMeeking et al. (2009). The composition of emitted smoke particles was continuously monitored across evolving flaming and smoldering combustion conditions using the AMS, which has been described in detail elsewhere (Canagaratna et al. 2007; DeCarlo et al. 2006). The fuel was burned under a 1.5 m diameter exhaust stack and the smoke forced up the stack to ~16 m above ground where emissions cool to near ambient conditions. A high-volume air pump pulled diluted smoke emissions from the

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top of the stack to the AMS through a 3.2 cm diameter, 20 m long stainless steel tube. A typical time from biomass combustion to smoke particle analysis by the AMS was ∼30 s. The "W" ion path was used to provide higher spectral resolution of measured ion fragments. Collected data (∼30 s resolution) were analyzed using AMS data analysis software (SQUIRREL and PIKA) (DeCarlo et al. 2006; Sueper 2009). Details about identification and quantification of smoke marker species measured are provided in the online supplemental information.

3. RESULTS AND DISCUSSION

Biomass burning emissions of gases and particles depend strongly on the combustion conditions, which can be broadly classified as flaming or smoldering. The combustion conditions can be monitored using the modified combustion efficiency (MCE), a ratio of emitted CO_2 to the sum of emitted CO_2 and CO (Chen et al. 2007; McMeeking et al. 2009; Yokelson et al. 1997). In this study MCE values larger than 0.9 and less than 0.8 were used to determine a predominance of flaming or smoldering combustion, respectively. An example timeline of MCE and key particle species emissions is provided in the online supplemental information.

3.1. Emission of Primary Smoke Markers

Previous studies have observed that potassium emission is higher in flaming-dominated combustion (e.g., Echalar et al. 1995) and that levoglucosan emissions are higher during lower temperature (smoldering) burns (Shafizadeh 1982). In order to be most useful as a marker for emissions of primary particle mass (or organic aerosol (OA), which often dominates particle mass), an ideal marker would be emitted at a constant ratio to total particle mass (or OA) across combustion phases and for different biomasses.

Ratios of K^+ and $C_2H_4O_2^+$ to particle mass measured by the AMS in the flaming and smoldering phases of individual burns are shown in Figure 1a. K^+ was typically emitted at a higher mass fraction in flaming phase combustion; $C_2H_4O_2^+$ was emitted at similar ratios to particle mass in flaming and smoldering phases of most burns. These observations are consistent with the poor relationship between potassium and levoglucosan concentrations reported for FLAME filter samples (Sullivan et al. 2008). Further, Sullivan et al. (2008) reported only modest dependence of the ratio of levoglucosan to aerosol organic carbon on fuel type. Together, these observations suggest that levoglucosan and related products are more universal primary smoke markers than potassium, since they do not depend as strongly on fuel type or combustion conditions.

3.2. Relationships between Anhydrosugars, AMS $C_2H_4O_2^+$, and AMS OA

Levoglucosan is the most abundant thermal breakdown product of cellulose identified in smoke particles. The thermal degradation of cellulose and hemicellulose also produces other anhydrosugars, including mannosan, galactosan, arabinosan, and xylosan. Mass fragment *m/z* 60 is commonly used as a marker for biomass burning in the AMS, where typically one major ion ($C_2H_4O_2^+$) contributes to the observed signal as also observed in this dataset (see the online supplemental information, Figure S1).

Figure 1b presents the correlation between levoglucosan, or levoglucosan + mannosan + galactosan, as determined from filters (Sullivan et al. 2008), with organic-equivalent (Zhang et al. 2005) $C_2H_4O_2^+$ measured simultaneously by the AMS. Strong correlations are observed, with correlation coefficients (R^2) of 0.91 and 0.93, for the relationship with levoglucosan alone or the sum of three anhydrosugar concentrations, respectively. These results, together with the absence of substantial $C_2H_4O_2^+$ in most other non-biomass burning aerosol types, confirm that $C_2H_4O_2^+$ is a suitable AMS marker for primary particle emissions from biomass burning. Multiple field studies have shown that $C_2H_4O_2^+$ is present at a level of ∼0.3 % of total OA during periods without biomass burning influence (e.g., Aiken et al. 2009; Docherty et al. 2008). Mohr et al. (2009) found $C_2H_4O_2^+$ in AMS analysis of meat cooking aerosols and laboratory studies also indicate it can form in AMS analysis of longer chain alkanoic acids. Takegawa et al. (2007) used an AMS to study oxalic acid, several other larger diacids, and glyoxylic acid and found only minor amounts of *m/z* 60. As Takegawa et al. (2007) discuss, fragmentation patterns in the AMS can differ from standard 70 eV EI spectra due to the higher vaporizer temperature used in the AMS. We hypothesize that the source of the ∼0.3% background $C_2H_4O_2^+$ in ambient OA is dominated by acid groups from SOA with a minor contribution from other sources such as meat cooking. The general representativeness of this background value should be evaluated in additional studies.

AMS analyses of levoglucosan, mannosan, and galactosan standards in our laboratory reveal that $C_2H_4O_2^+$ comprises 14.1, 13.8, and 12.1% of the total ion fragment pattern, respectively (Aiken et al. (2009), Schneider et al. (2006), and Alfarra et al. (2007) previously reported values of approximately 13%, 12%, and 8% for levoglucosan, respectively). Using this information, and assuming for the moment that no other molecules in the smoke particles generate $C_2H_4O_2^+$, we can calculate an AMS "anhydrosugar-equivalent mass concentration" (anhyd.-eq. conc.), defined as the sum of the levoglucosan, mannosan, and galactosan concentrations required to produce the observed $C_2H_4O_2^+$ signal intensity. We calculate the anhyd.-eq. conc. by multiplying the observed $C_2H_4O_2^+$ mass concentration by 7.5 to account for the full anhydrosugar fragment pattern. The results of these calculations are shown in Figure 1c, where the anhyd.-eq. conc. is plotted vs. the sum of the three anhydrosugar concentrations from simultaneous filter samples. If levoglucosan, mannosan, and galactosan were the only molecules in the smoke particles to yield $C_2H_4O_2^+$, we would expect the anhyd.-eq. conc. to equal the concentration sum of these three species. Clearly this is not the case. The slope of a best fit line for this dataset is 8.5 with a small intercept, indicating that the AMS $C_2H_4O_2^+$

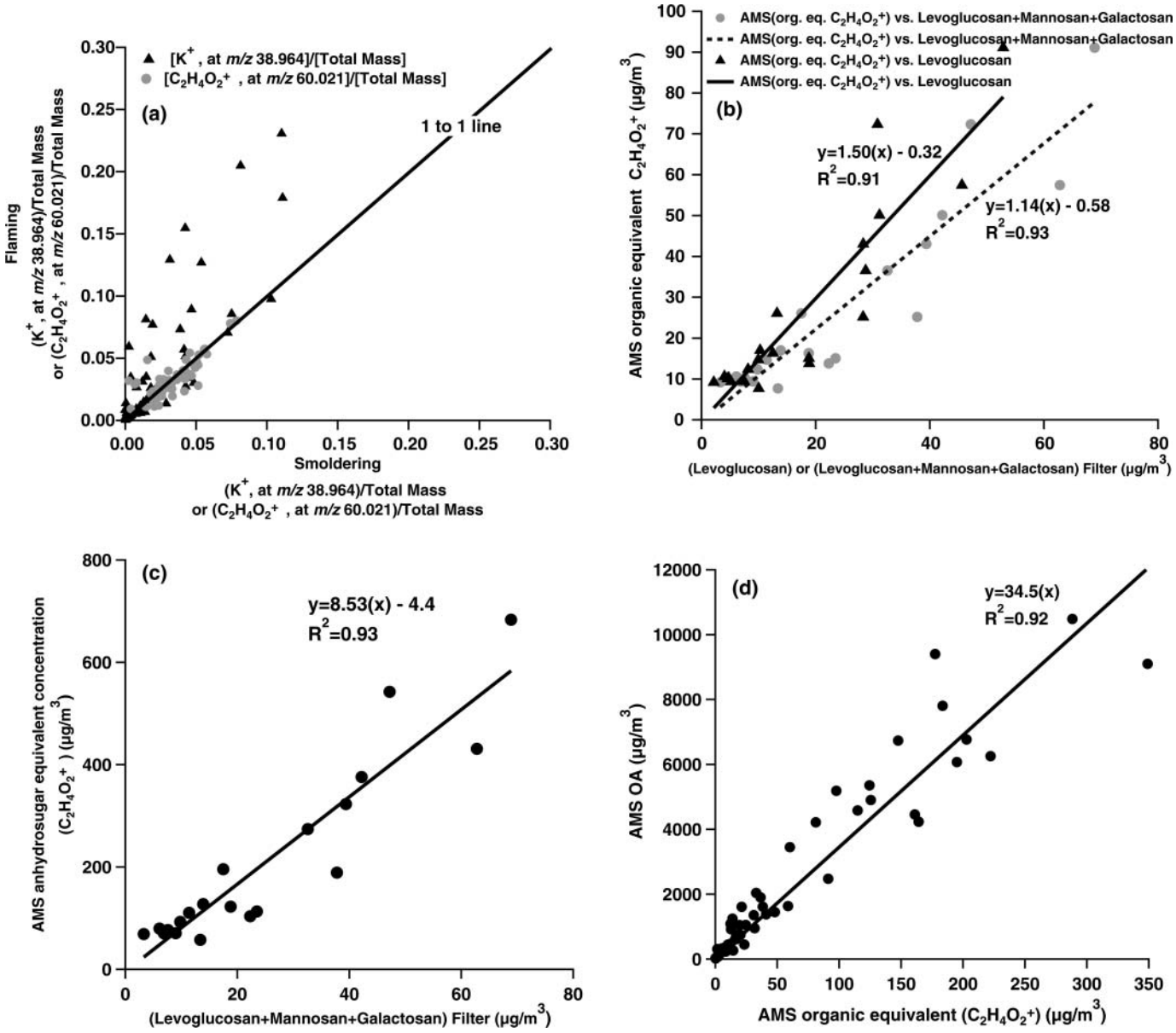

FIG. 1. Observations of smoke particles during FLAME II open biomass burning experiments: (a) comparisons of the ratios of K^+ (at *m/z* 38.964) and $C_2H_4O_2^+$ (at *m/z* 60.021) to total AMS particle mass for flaming and smoldering fire phases of individual FLAME II burns; (b) relationship of organic equivalent concentrations of $C_2H_4O_2^+$ from the AMS to the concentration of levoglucosan or the concentration sum of levoglucosan, mannosan, and galactosan measured from simultaneously collected filter samples (Sullivan et al. 2008); (c) a hypothetical computed AMS anhydrosugar-equivalent concentration (determined as 7.5 times AMS $C_2H_4O_2^+$) to levoglucosan + mannosan + galactosan concentrations measured in simultaneously collected filter samples; (d) AMS organic aerosol concentration vs. AMS $C_2H_4O_2^+$ organic equivalent concentration for individual FLAME II burns. The plotted points in each panel represent the average values measured, typically over several minutes of sampling. The orthogonal distance regression approach was used to compute best fit lines in panels (b)–(d).

signal is much larger than can be explained by the three measured anhydrosugars. This is not surprising. Other structurally similar molecules, which are likely abundant in smoke, also produce $C_2H_4O_2^+$ upon electron impact fragmentation. AMS laboratory tests reveal, for example, that glucose yields an important fragment at $C_2H_4O_2^+$, comprising ~10% of the total ion fragment pattern.

We can also directly investigate the utility of AMS $C_2H_4O_2^+$ itself as a smoke marker by examining the correlation between OA and $C_2H_4O_2^+$ across all FLAME II burns. A correlation of $R^2 = 0.92$ with a slope of 34.5 between biomass burning OA and $C_2H_4O_2^+$ was observed (Figure 1d), similar to the relationship determined by Aiken et al. (2009) for mostly unprocessed smoke reaching downtown Mexico City from nearby forest fires.

Alfarra et al. (2007) previously proposed a ratio of 36 for domestic wood burning in Zurich and indicate a ratio of 30 was estimated for summertime biomass (presumably open) burning in the region. Weimer et al. (2007) report a much more variable range of this ratio for their residential wood burning experiments and a tendency for lower OA to m/z 60 ratios during flaming conditions.

The correlation between OA and $C_2H_4O_2^+$ observed here is stronger than the correlation between FLAME filter-based measurements of levoglucosan and OC ($R^2 = 0.68$) (Sullivan et al. 2008). One possible explanation for the improved relationship is that $C_2H_4O_2^+$ appears to reflect a broader range of biomass burning molecules than the three anhydrosugars discussed here. The sum of all compounds yielding $C_2H_4O_2^+$ may define a more constant fraction of emitted fine particle OA than does levoglucosan. As Sullivan et al. (2008) point out, the levoglucosan/OC yield appears to vary across fuel components (e.g., branches, needles/leaves, grasses, etc.) in accordance with changes in the fuel mass fraction of cellulose. The less variable ratio of OA to $C_2H_4O_2^+$ observed here suggests that increases (decreases) in levoglucosan yield in biomass burning smoke may be offset to some extent by corresponding decreases (increases) in other molecules that also yield $C_2H_4O_2^+$ in the AMS.

The strength of the OA vs. $C_2H_4O_2^+$ relationship in fresh smoke across fuel types and combustion conditions offers promise that AMS measurements may be useful for directly estimating contributions of biomass burning primary emissions to ambient fine particle organic carbon. Additional research is necessary, however, to assess this relationship as a function of other biomass burning source types (e.g., residential wood burning) and various atmospheric processes, including smoke dilution (which may affect organic gas-particle partitioning) and smoke plume aging.

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