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Online molecular characterization of fine particulate matter in Port Angeles, WA: Evidence for a major impact from residential wood smoke

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HIGHLIGHTS

- A novel analytical technique was used to quantify wood smoke markers in near real-time.
- Levoglucosan, nitroaromatics, and methoxyphenols dominated PM, particularly at night.
- Residential wood smoke is a major source of wintertime PM in Port Angeles, WA.
- Levoglucosan forms low volatility products in the presence of acids.

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ABSTRACT

We present on-line molecular composition measurements of wintertime particulate matter (PM) during 2014 using an iodide-adduct high-resolution, time-of-flight chemical ionization mass spectrometer (HR-TOF-CIMS) coupled to a Filter Inlet for Gases and AEROsols (FIGAERO). These measurements were part of an intensive effort to characterize PM in the region with a focus on ultrafine particle sources. The technique was used to detect and quantify different classes of wood burning tracers, including levoglucosan, methoxyphenols, and nitrocatechols, among other compounds in near real-time. During the campaign, particulate mass concentrations of compounds with the same molecular composition as levoglucosan ranged from 0.002 to 19 $\mu g/m^3$ with a median mass concentration of 0.9 $\mu g/m^3$. Wood burning markers, in general, showed a strong diurnal pattern peaking at night and in the early morning. This diurnal profile combined with cold, stagnant conditions, wind directions from predominantly residential areas, and observations of lower combustion efficiency at night support residential wood burning as a dominant source of wintertime PM in Port Angeles. This finding has implications for improving wintertime air quality in the region by encouraging the use of high efficiency wood-burning stoves or other cleaner home heating options throughout the relevant domain.

1. Introduction

In the U.S. Pacific Northwest, PM episodes that approach or exceed regulatory air quality thresholds often occur in the wintertime, due to suppressed vertical mixing and local emissions (Hand et al., 2012; Larson et al., 2004; Ogulei, 2010). Winter episodes occur on synoptic timescales, associated with prolonged cold periods and shallow mixed layers, particularly during nighttime, which promote enhanced residential heating often by wood stoves and fireplaces. However, direct compositional links to residential biofuel sources during these episodes are lacking.

Pollution events induced from residential wood burning emissions are globally important for both human health and climate (Fine et al., 2004; Gorin et al., 2006; Hedberg et al., 2006; Khalil and

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Rasmussen, 2003; Larson et al., 2004; Naeher et al., 2007; Ogulei, 2010; Rogge et al., 1998; Schauer and Cass, 2000; Szidat et al., 2007; Ward et al., 2006). Exposure to wood smoke particles is associated with decreased lung function, asthmatic symptoms, and is estimated to be responsible for 1–2 million premature deaths annually (Bolling et al., 2009; Naeher et al., 2007). Further, black carbon and light-absorbing "brown" carbon released from wood burning impact climate by strongly absorbing light and affecting budgets of cloud condensation and ice nuclei (Carrico et al., 2010; Mohr et al., 2013; Petters et al., 2009; Ramanathan and Carmichael, 2008; Saleh et al., 2014; Sun et al., 2007; Weimer et al., 2009). The impact of wood combustion on human health and climate underscore the need to better understand and characterize various sources of wood smoke PM.

Flaming and smoldering combustion conditions volatilize and thermally breakdown compounds found in plant material—namely cellulose, hemicelluloses, lignin, proteins, and plant waxes—forming compounds that can act as unique wood smoke tracers in PM (Andreae and Merlet, 2001). The most universally used tracer for biomass burning is levoglucosan, formed from the combustion of cellulose (Fine et al., 2002; Fraser and Lakshmanan, 2000; Hennigan et al., 2010; Hoffmann et al., 2010; Nolte et al., 2001; Rogge et al., 1998; Simoneit et al., 1999; Sullivan et al., 2014). Levoglucosan represents a significant fraction of PM impacted by residential wood combustion during winter. This compound is one of the most abundant individual organic compounds found in atmospheric aerosols (Fine et al., 2002; Nolte et al., 2001). However, levoglucosan provides little detail about the type of biomass burning (e.g., woodstove vs. fireplace vs. open biomass burning), combustion conditions (e.g., flaming vs. smoldering), and fuel being combusted, which are all needed to accurately apportion the various biomass burning related sources of PM. Guaiacol- and syringol-derived methoxyphenols, produced from the pyrolysis of lignins, and resin acids are typically used to distinguish between softwood (e.g., conifers such as pine) and hardwood combustion (e.g., oak) (Edye and Richards, 1991; Hawthorne et al., 1992; McDonald et al., 2000; Rogge et al., 1998; Schauer and Cass, 2000; Schauer et al., 2001; Simoneit, 2002; Simoneit et al., 1993; Simpson et al., 2005). In addition to levoglucosan and methoxyphenols, other wood smoke compounds used as chemical tracers include plant wax esters, carboxylic acids, and toxic compounds including polycyclic aromatic hydrocarbons (PAHs), nitrophenols, nitrocatechols, nitriles, and amides (Elias et al., 1999; Harrison et al., 2005; Iinuma et al., 2010; Ma and Hays, 2008; Mohr et al., 2013; Oros and Simoneit, 2001; Simoneit, 2002; Simoneit et al., 1993, 2003).

A key challenge associated with quantifying chemical tracers in wood smoke is a lack of methods that can unambiguously identify and quantify multiple highly oxygenated and nitrogen-containing markers with a time resolution capable of distinguishing between common time-varying sources such as traffic, home heating, and combustion phases. Chemical measurements of wood smoke PM have typically been off-line, involving the collection of PM on filters for several hours, followed by extraction and analysis using gas chromatography (GC) (Bari et al., 2009; Edye and Richards, 1991; Elias et al., 1999; Fine et al., 2004; Fraser and Lakshmanan, 2000; Hawthorne et al., 1992; Hedberg et al., 2006; Ma and Hays, 2008; McDonald et al., 2000; Nolte et al., 2001; Oros and Simoneit, 2001; Rogge et al., 1998; Schauer and Cass, 2000; Schauer et al., 2001; Simoneit et al., 1993; Simpson et al., 2005). This method is quantitative and well-suited for analyzing hydrocarbons; however, the drawbacks include the sample preparation, which involves extraction and derivatization of oxygenated and high molecular weight compounds, unresolved complex mixtures (UCM), and low time resolution. Recently, Engling and co-workers developed a liquid-based method for improved quantification of oxygenated compounds in biomass burning aerosol, namely levoglucosan, using high performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD) (Engling et al., 2006). This technique requires no sample preparation or derivatization, has faster separation than GC, and a low limit of detection (Christian et al., 2010; Engling et al., 2006; Gorin et al., 2006; Sullivan et al., 2014). Electrospray ionization-mass spectrometry (ESI-MS) has recently been used to detect high molecular weight oxygenated and nitrogen-containing polar compounds found in biomass burning aerosol that cannot be detected by GC-MS (Laskin et al., 2009; Smith et al., 2009), but lacks reproducible quantification. While both HPAEC-PAD and ESI-MS methods have improved the detection of polar compounds found in wood smoke particles, neither technique, as employed so far, provides high time resolution. Online techniques, such as aerosol mass spectrometry (AMS), have been used with positive matrix factorization (PMF) to quantify biomass burning aerosol in real-time (Aiken et al., 2010; Weimer et al., 2008); however, the technique utilizes electron impact ionization resulting in extensive fragmentation, which precludes detection and identification of specific molecular tracers.

Here we present measurements of ambient fine PM using high-resolution, time-of-flight chemical ionization mass spectrometry (HR-TOF-CIMS) coupled to a Filter Inlet for Gases and AEROsols (FIGAERO) (Lopez-Hilfiker et al., 2014). This online technique combines soft ionization with a high-resolution, time-of-flight mass analyzer allowing the detection and quantification of oxygenated and nitrogen-containing compounds on the molecular level at near real-time with no sample preparation (Lee et al., 2014; Lopez-Hilfiker et al., 2014). Further, gas- and particle-phase compounds are detected simultaneously with this technique, and particulate compounds are thermally resolved providing additional information on volatility. A predecessor of this technique was used to quantify nitrophenols in submicron PM in Detling, UK at hourly time resolution (Mohr et al., 2013). In this work, diel transformations and volatility relevant to wood burning organic aerosol are probed by simultaneously detecting compounds with molecular compositions consistent with levoglucosan, methoxyphenols, nitrophenols, resin acids, lignans, and other oxygenated and nitrogen-containing markers in wood smoke particles. We provide insight into the dominant sources of fine PM during several poor air quality episodes in Port Angeles, WA.

2. Materials and methods

Measurements were conducted in Port Angeles, WA at the Port Angeles Fire Station. The site is located at 48.115°N, 123.436°W (see Figure S1 of the Supporting Information (SI) for a site map of the location). Residential communities are primarily to the south and southwest while industrial and port sources are to the north of this site. Continuous measurements of gases, particle size distributions and mass concentrations, and meteorological conditions have been conducted at this site since December 2013. Gas-phase measurements of CO (Thermo Fisher Scientific, Model 48C TLE) and CO_2 (LI-COR Inc., Model LI-840A) that were zeroed every 2 h and calibrated daily and measurements of $PM_{2.5}$ using an optical particle counter (OPC, MetOne Model 212 Profiler) were conducted during this intensive campaign. Additional details can be found in the SI; we focus on measurements made using HR-TOF-CIMS described below.

2.1. FIGAERO HR-TOF-CIMS measurements

An iodide-adduct high-resolution, time-of-flight chemical ionization mass spectrometer (HR-TOF-CIMS) (Lee et al., 2014) operated with a custom-built Filter Inlet for Gases and AEROsols