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Transport, biomass burning, and in-situ formation contribute to fine particle concentrations at a remote site near Grand Teton National Park

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HIGHLIGHTS

- Particulate matter at Grand Teton National Park characterized using HR-ToF-AMS.
- In-situ formation of oxygenated OA (61% PM1); transported biomass-burning OA (14%).
- Transport of ammonium (9%) and sulfate (13%) from populated areas to S. and W.
- Daytime organic nitrogen contains nitriles/pyridines, with amine fragments at night.
- Historical data suggest that these characteristics are typical of summer conditions.

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ABSTRACT

Ecosystem health and visibility degradation due to fine-mode atmospheric particles have been documented in remote areas and motivate particle characterization that can inform mitigation strategies. This study explores submicron (PM_1) particle size, composition, and source apportionment at Grand Teton National Park using High-Resolution Time-of-Flight Aerosol Mass Spectrometer data with Positive Matrix Factorization and MODIS fire information. Particulate mass averages 2.08 $\mu g/m^3$ (max = 21.91 $\mu g/m^3$) of which 75.0% is organic; PMF-derived Low-Volatility Oxygenated Organic Aerosol (LV-OOA) averages 61.1% of PM_1 (or 1.05 $\mu g/m^3$), with sporadic but higher-concentration biomass burning (BBOA) events contributing another 13.9%. Sulfate (12.5%), ammonium (8.7%), and nitrate (3.8%) are generally low in mass. Ammonium and sulfate have correlated time-series and association with transport from northern Utah and the Snake River Valley. A regionally disperse and/or *in situ* photochemical LV-OOA source is suggested by 1) afternoon concentration enhancement not correlated with upslope winds, anthropogenic NO_x, or ammonium sulfate, 2) smaller particle size, higher polydispersity, and lower levels of oxidation during the day and in comparison to a biomass burning plume inferred to have traveled ~480 km, and 3) lower degree of oxidation than is usually observed in transported urban plumes and alpine sites with transported anthropogenic OA. CHN fragment spectra suggest organic nitrogen in the form of nitriles and/or pyridines during the day, with the addition of amine fragments at night. Fires near Boise, ID may be the source of a high-concentration biomass-burning event on August 15–16, 2011 associated with SW winds (upslope from the Snake River Valley) and increased sulfate, ammonium, nitrate, and CHN and CHON fragments (nominally, amines and organonitrates). Comparison to limited historical data suggests that the amounts and sources of organics and inorganics presented here typify summer conditions in this area.

1. Introduction

Fine particles are involved in climate and environmental effects including direct and indirect radiative forcing, nutrient deposition,

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visibility degradation, and human health effects, much of which is attributed to anthropogenic emissions (Stocker et al., 2013). As a result, many particle source apportionment studies focus on urban areas. Urban pollution is transported widely into downwind ecosystems (e.g. Van Donkelaar et al., 2008; Zhang et al., 2007), but cities account for only 0.5–2.5% of land surface (Schneider et al., 2010), leaving air quality in many regions uncharacterized. Remote sensing, basic measurement networks such as IMPROVE in the U.S. (Malm and Hand, 2007), and models help to fill in these gaps in terms of particle concentrations, finding that organic aerosol (OA) are a significant fraction of fine particulate mass (Hand et al., 2012; Zhang et al., 2007). However, the sophisticated source apportionment studies need for effective mitigation (and model validation) in remote areas are less common.

Many remote environments are also especially sensitive to nutrient deposition, which can arise from, for example, gaseous or particulate nitrogen species and result in soil nutrient leaching, eutrophication, water-body acidification, and reduced plant hardiness, among other effects (Fenn et al., 2003). Non-nutrient species, such as some organics, can also be involved in chemistry leading to long-range transport and deposition. In Rocky Mountain National Park (RMNP), for instance, deposited nitrogen (mainly in the form of precipitation) is associated with organics transported into the park from neighboring cities (Benedict et al., 2013; Day et al., 2012; Schurman et al., 2015). Fine particles can also contribute to visibility degradation (Levin et al., 2009; Malm and Hand, 2007).

Organic nitrogen (ON) is also of concern, as it comprises roughly one-fifth to one-third of fine particulate mass worldwide and contributes significantly to total nitrogen deposition in RMNP and elsewhere (Cape and Cornell, 2011; Beem et al., 2010). ON compounds found in aerosols include amines and imines, uric, amino, and other organic acids, and organic nitrates (Cape and Cornell, 2011). Like emissions of inorganic nitrogen, which more than doubled since the 1970s, environmental levels of organic nitrogen species have been increasing (Galloway et al., 2008).

At Grand Teton National Park (GTNP), past work indicates large upwind nitrogen emissions (Clarisse et al., 2009) and deposition (Fenn et al., 2003) with clear ecological detriment including lake acidification and diatom species shifts (Saros et al., 2010). The detrimental effects outlined above and lack of prior particle characterization at GTNP motivate the PM_1 source apportionment work presented here.

In general, particle sources in remote areas appear to be complex; biogenic OA is important and often formed from reactions between biogenic volatile organic carbon species (BVOCs) and anthropogenic pollutants (Hoyle et al., 2011); high concentrations of particles and gaseous precursors can also be transported from urban areas. In the RMNP study mentioned above, biomass burning, transport of anthropogenic particles with mountain-valley circulations, and secondary biogenic sources all contributed significantly to fine PM (Schurman et al., 2015); similar patterns have been observed at Whistler Mountain in Canada (Gallagher et al., 2011).

Particle sources can be explored through a combination of composition and meteorological data. For instance, sulfate and nitrate precursors have important anthropogenic sources, and thus if found in an uninhabited area indicate long-range transport. The oxidation level of organic species can also reveal the degree of atmospheric aging. Metrics such as *f*43 (the ratio of mass at *m/z* 43 to total organic mass) and *f*44 (as for *f*43, but for *m/z* 44) are indicative of relative carbonyl/hydrocarbon ($C_2H_3O^+$ and/or $C_3H_7^+$) and carboxylic acid (CO_2^+) content, respectively (Zhang et al., 2011). Ambient aerosols generally progress toward higher *f*44 and lower *f*43 as they are oxidized (Ng et al., 2011). Statistical techniques such as Positive Matrix Factorization are used to explore combinations of aerosol components common at a given site and can be combined with meteorological measurements and/or models to indicate geographical sources of a given particle composition type (Paatero and Tapper, 1994).

However, in order to connect rapid changes in particle composition with meteorological data, the techniques outlined above require higher time resolution than that offered by filter sampling, which can be especially limited (~24 h) in low-mass environments such as GTNP. To this end, an aerosol mass spectrometer with 2–5 min time resolution was deployed as part of the Grand Teton Reactive Nitrogen Deposition Study (GrandTReNDS) with the goal of exploring OA sources, especially as they inform nitrogen deposition. The results are compared to historical particulate matter and fire data to determine whether the particle sources found here represent 'typical' local conditions during summer.

2. Methods

2.1. Instrumentation and analysis

An Aerodyne High-Resolution Time-of-Flight Aerosol Mass Spectrometer (AMS) was used to quantitatively measure the size and non-refractory composition of submicron particles. Briefly, the AMS separates gases and particles by vacuum diffusion differential, separates particle sizes by inertia in a particle flight region, vaporizes the particles at 600 °C, ionizes the fragments under 70 eV electron impact, and detects the ions using time-of-flight mass spectrometry; the AMS has been discussed in depth elsewhere (Decarlo et al., 2006). The aerodynamic lens preceding the interior vacuum transmits particles ~60 nm < D_p < ~700 nm (Liu et al., 2007), encompassing the vast majority of submicron particulate mass measured by a differential mobility particle sizer (DMPS) during this study (Ezra Levin, personal communication, 17 August, 2012; Fig. S1). Co-located instrumentation included a particle sizing rack with an aerodynamic particle sizer (APS, TSI 3021), optical particle counter (OPC, LASAIR 1003), and DMPS (TSI 3085), a gas measurement rack with CO (Teledyne-API Inc., Model 300EU), NO, NO_x, NO_y (Teledyne-API Inc., Models 200EU and Model 201E) and two ammonia (NH_3) measurements (Particle Measuring Systems Air Sentry II Ion Mobility Spectrometer & Picarro G1103 Analyzer), and a Climatronics All-In-One Weather Sensor (Part Number 102780) measuring wind direction and speed, temperature, and relative humidity. 24- and 12-h URG denuder/filter-pack samples were used to characterize gaseous ammonia and nitric acid and $PM_{2.5}$ ion concentrations. Methodological details and results from some of these measurements can be found in Prenni et al. (2014) and Benedict et al. (2013).

The AMS collected 2–5 min average particle mass spectra spanning *m/z* 12- *m/z* 300 for V (high sensitivity), W (high resolution), and PToF (particle sizing) modes (see Decarlo et al., 2006). Ionization efficiency calibrations using 300 nm ammonium nitrate particles were performed once or more per week with verification against an in-line condensation particle counter (CPC, TSI model 3010). Gaseous CO_2 contributions to *m/z* 44 were quantified using an in-line Li-COR CO_2 monitor (LI-820). Data analysis utilized SQUIRREL (v1.51H), PIKA (v1.10H; Sueper, 2013; using the updated fragmentation table from Aiken et al., 2008), and the PMF2 algorithm (Paatero and Tapper, 1994) in PET (v2.03A,Ulbrich et al., 2009) in Igor Pro 6.22A (WaveMetrics Inc., Lake Oswego, OR). High-resolution data are available July 27 19:00 through the end of the study.

Quantifying organic nitrogen via AMS is complicated by the ionization-induced fragmentation of nominally 'nitrate' (NO_n^+) and 'ammonium' (NH_n^+) ions from organic parent compounds (broadly, organonitrates and amines, respectively) under ionization (Farmer