



## Soil humic-like organic compounds in prescribed fire emissions using nuclear magnetic resonance spectroscopy



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### ABSTRACT

Here we present the chemical characterization of the water-soluble organic carbon fraction of atmospheric aerosol collected during a prescribed fire burn in relation to soil organic matter and biomass combustion. Using nuclear magnetic resonance spectroscopy, we observed that humic-like substances in fire emissions have been associated with soil organic matter rather than biomass. Using a chemical mass balance model, we estimated that soil organic matter may contribute up to 41% of organic hydrogen and up to 27% of water-soluble organic carbon in fire emissions. Dust particles, when mixed with fresh combustion emissions, substantially enhances the atmospheric oxidative capacity, particle formation and microphysical properties of clouds influencing the climatic responses of atmospheric aerosol. Owing to the large emissions of combustion aerosol during fires, the release of dust particles from soil surfaces that are subjected to intense heating and shear stress has, so far, been lacking.

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### 1. Introduction

Particulate organic carbon (POC) in fire emissions has been regularly attributed to biomass combustion (Hoffer et al., 2006; Decesari et al., 2006) with water-soluble humic-like substances (HULIS) accounting for a large fraction of POC. Meanwhile, the resuspension of mineral particles in fires due to enhanced turbulent mixing near and after the burn front was previously observed (Clements et al., 2008) and some similarities with terrestrial organic matter were observed (Stone et al., 2009; Kavouras et al., 2012). When dust particles are mixed with biomass burning emissions, the overall oxidative capacity (i.e. reactions) and new particle formation potential of the smoke plume is enhanced influencing the formation of cloud condensation nuclei (DeMott et al., 2003). Fires have a detrimental effect on ecosystems and the atmosphere, near and far away from the area of the burn (Certini, 2005; Chen et al., 2009). More frequent, larger and more

destructive wildfires due to recurrent and long-lasting droughts, longer fire seasons and changes in biomass have been observed over the last few decades (Gedalof et al., 2005; Keeley et al., 1999). Areas with the greatest fire frequency include the Arc of Deforestation in Brazil, sub-Saharan and southeastern Africa, Australia, southeastern and western US, southeast Asia, the southern plains of Siberia and deserts in Mongolia and China (Giglio et al., 2006). In these regions, the fire season lasts, on average, six months, although longer periods (8–12 months) were observed in the savannahs of Africa, eastern Australia, the US and Brazil. Many of these regions have also been characterized by soil textures that are prone to wind erosion contributing ~1500 Tg/yr of dust particles (Maria et al., 2004).

The heating of soil during a fire can modify the physical and chemical properties of soil textures by forming coarse soil particles through mineralization and by producing lipophilic layers due to pyrolysis of soil organic matter, increasing the potential for wind erosion (Atanassova and Doerr, 2011). These effects were more evident in deserts and shrublands as compared to grass and forest fires due to soil heating and differences in soil stability (Cruz et al., 2011). Studies of physical properties of soils before and after fires

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in arid and semi-arid areas often show an increase in soil bulk density, disaggregation of soil structure, and collapse of pores, at least in part a result of destruction of organic binding agents (Kennard and Gholz, 2001).

The heating in and around the fire front has been shown to generate sufficient turbulence and wind shear to trigger the suspension of loose dust particles into the atmosphere (Clements et al., 2008). In a recent study, we identified that soil minerals may contribute up to 10% of PM<sub>10</sub> (particles with aerodynamic diameter less than 10 μm) emissions from prescribed fires (Kavouras et al., 2012). An organic carbon-to-organic mass (OM/OC) conversion factor of 3.1, comparable to OM/OC values for mineral soils in the US (Cambardella et al., 2001), was used to reconstruct aerosol mass when soil contribution was the highest. The conversion factor was associated with the increased content in humic and fulvic acids. These compounds have been found to modify the indirect aerosol climate forcing by changing the critical size and super-saturation of cloud condensation droplets (Kokkola et al., 2006). Aerosol containing humic acids was also shown to influence atmospheric oxidation such as the conversion of NO<sub>2</sub> to nitrous acid (HONO) (Wang et al., 2003). At the Gleason prescribed fire, impacts of the fire included progressive breakdown of soil structure over slightly more than one year that resulted in disaggregated soil particles at the soil surface and into the soil column that contributed to higher post-fire soil aeolian suspension potential; and decreased water infiltration potential (Chief et al., 2012).

This paper presents, for the first time, the *in-situ* chemical profiles of particulate water-soluble organic carbon (WSOC) emissions from a prescribed burn event and their relationships to soil organic matter and biomass combustion. By applying the similarity index and the chemical mass balance model, we calculate the contribution of soil and biomass combustion particles to prescribed burn WSOC emissions in order to identify which components of soil organic matter are present in the fire plume and whether turbulence in the fire front and/or temperature-induced structural changes enhance the resuspension of soil organic matter.

## 2. Materials and methods

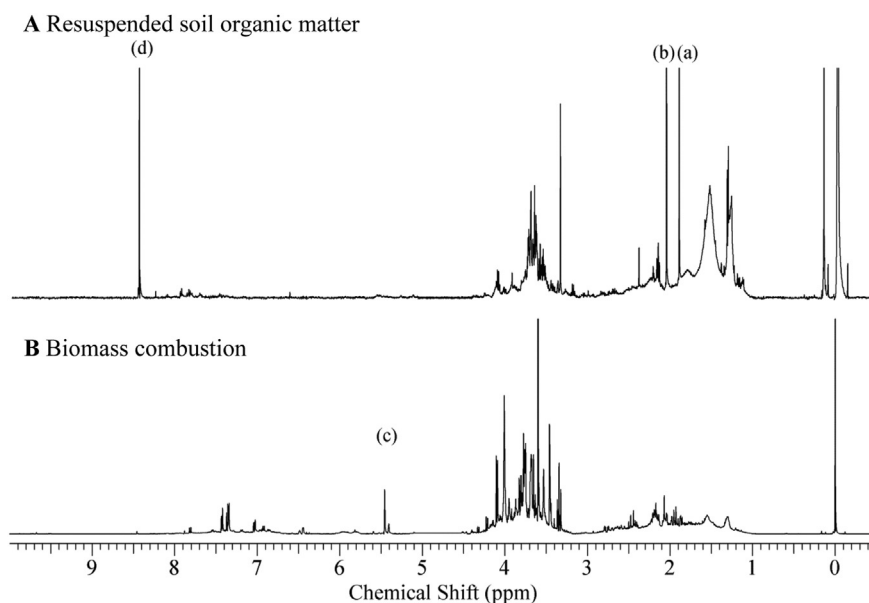
The prescribed burn extended over an area of 1.55 km<sup>2</sup> covered by sagebrush (*Artemisia* sp.) and pinyon pine/juniper (*Pinus monophylla* and *Juniperus*

*osteosperma*) plant communities in the Upper Gleason watershed within the Great Basin Desert in east-central Nevada (39°23'43"N, 115°03'57"W). The fire was ignited with a heavy drip-torch starting at the southern boundary of the plot (heading fire). It lasted for approximately 6 h with soil temperatures reaching 315 °C at a 1-cm depth under the sagebrush canopy. Measurements included: (i) the collection of time-resolved PM<sub>10</sub> aerosol samples on Teflon and quartz filters during the prescribed burn event using the In-Plume Emission Test Stand (IPETS) (Nussbaum et al., 2009), corresponding to 0–2 h, 2–4 h and 4–6 h after the initial ignition (hereafter, Rx#1, Rx#2 and Rx#3, respectively); (ii) PM<sub>10</sub> soil dust before and after the prescribed burn event using the Portable In-Situ Wind Erosion Laboratory (PI-SWERL) (Etyemezian et al., 2007); and (iii) PM<sub>10</sub> aerosol samples from the combustion of ~2 m<sup>3</sup> of native biomass in a heavy-duty metal fire pit for 2 h (biomass combustion, hereafter). Samples were analyzed for elements, ions, elemental carbon, total organic carbon and WSOC. A portion (half) of the collected filters was extracted in H<sub>2</sub>O and analyzed by NMR.

The IPETS sampling system was located on the north boundary of the prescribed burn plot (winds blowing from the south at less than 10 m/s). PM<sub>10</sub> aerosol samples of resuspended soil dust (on both Teflon and quartz filters) were also collected from eight locations inside the prescribed burn plot before the event using the PI-SWERL system. The WSOC was determined by thermal optical reflectance method. A portion (half) of the quartz filter was sonicated in ultrapure H<sub>2</sub>O for 1 h. The extract was dried and re-dissolved in 0.5 ml D<sub>2</sub>O containing 30 μg of 3-(trimethylsilyl)propionic acid-d<sub>4</sub> sodium salt (TSP-d<sub>4</sub>) internal standard and transferred to 5 mm diameter NMR tubes. <sup>1</sup>H NMR spectra were obtained on Bruker NMR spectrometers with operating frequencies of 500 and 600 MHz at 298 K using spin-lock, acquisition time of 2 s, relaxation delay of 1 s and 1 Hz exponential line broadening (8192 acquisitions). A suppression sequence using 90-degree selective pulses for water was applied to eliminate the water signal interference. The baseline was manually corrected and integrated using the ACD/NMR processor (Version 12.01 Academic Edition). The identification was done based on their chemical shift (δ) relative to that of TSP-d<sub>4</sub> set at 0.0 ppm. Because of atmospheric H<sub>2</sub>O residues in the sample, the segment from ~4.5 to ~5.0 ppm was removed from all NMR spectra. We applied the *icoshift* algorithm to align the NMR spectra (Savorani et al., 2010) and integrated the intensity of signals in 250 pre-defined bins with 0.04 ppm width. A portion of the NMR spectrum was excluded because of water suppression and low signal-to-noise ratios; thus, the number of variables was reduced to 236.

## 3. Results and discussion

NMR spectroscopy has recently been used to qualitatively determine the chemical content of the water soluble fraction of biogenic, marine and background organic aerosol (Decesari et al., 2006, 2011; Tagliavini et al., 2006; Ziemba et al., 2011). The NMR spectra of native soil (from samples collected prior to the burn) organic matter and biomass combustion are illustrated in Fig. 1. The



**Fig. 1.** 600 MHz <sup>1</sup>H NMR of resuspended (by PI-SWERL) soil organic matter (A) and biomass combustion (B). The segment from ~4.5 to ~5.0 ppm was removed from all NMR spectra due to H<sub>2</sub>O residues. The peaks (a), (b) and (d) were uniquely identified in soil organic matter extract but not assigned to a specific compounds. The peak (c) was tentatively assigned to levoglucosan, a tracer of wood burning.

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