

Volatile and semivolatile organic compounds in laboratory peat fire emissions



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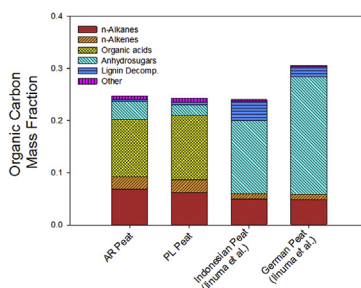
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HIGHLIGHTS

- Volatile and semivolatile organics were measured in peat fire emissions.
- Hazardous air pollutants represented ~60% of speciated VOC emissions.
- PM_{2.5} organic acid emissions from peat fires were reported for the first time.
- Estimated peat wildfire emissions were compared with National Emissions Inventory.

GRAPHICAL ABSTRACT



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ABSTRACT

In this study, volatile and semi-volatile organic compound (VOCs and SVOCs) mass emission factors were determined from laboratory peat fire experiments. The peat samples originated from two National Wildlife Refuges on the coastal plain of North Carolina, U.S.A. Gas- and particle-phase organic compounds were quantified by gas chromatography-mass spectrometry and by high pressure liquid chromatography. Hazardous air pollutants (HAPs) accounted for a large fraction (~60%) of the speciated VOC emissions from peat burning, including large contributions of acetaldehyde, formaldehyde, benzene, toluene, and chloromethane. In the fine particle mass (PM_{2.5}), the following organic compound classes were dominant: organic acids, levoglucosan, *n*-alkanes, and *n*-alkenes. Emission factors for the organic acids in PM_{2.5} including *n*-alkanoic acids, *n*-alkenoic acids, *n*-alkanedioic acids, and aromatic acids were reported for the first time for peat burning, representing the largest fraction of organic carbon (OC) mass (11–12%) of all speciated compound classes measured in this work. Levoglucosan contributed to 2–3% of the OC mass, while methoxyphenols represented 0.2–0.3% of the OC mass on a carbon mass basis. Retene was the most abundant particulate phase polycyclic aromatic hydrocarbon (PAH). Total HAP VOC and particulate PAH emissions from a 2008 peat wildfire in North Carolina were estimated, suggesting that peat fires can contribute a large fraction of state-wide HAP emissions.

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1. Introduction

Peat fires are becoming a greater source of concern due to the immense potential of the resultant carbon emissions to influence climate (Frolking et al., 2011; Sherwood et al., 2013; Turetsky et al., 2011). Peat is an accumulation of partially decayed plant organic matter formed under water saturated wetland conditions over millennial timescales. Peatlands are considered an important global carbon sink, covering ~3% of the world's land surface yet storing approximately one third of surface terrestrial organic carbon (Joosten and Clark, 2002).

Peatlands are expected to become more vulnerable to wildfires due to changing land use activities (i.e. deforestation, drainage, land clearing fires) and exacerbated drought conditions due to climate change. Increased degradation of peat (e.g., from peat fires) and resulting carbon emissions may alter the role of peatlands in the global carbon cycle from a net carbon sink to a source to the atmosphere with potentially significant consequences for climate change. Peat wildfires are characterized as low temperature, smoldering combustion fires that are extremely difficult to extinguish and can continue smoldering for long periods (i.e. weeks to years). Because of these characteristics, they are deemed particularly pernicious environmental disturbances relative to other vegetation fire events. Furthermore, peat fires can propagate laterally and vertically, burning organic matter including underlying organic soil at greater depths and consuming up to 100 times more fuel per unit area than flaming fires (Rein, 2013).

Previous studies on peat fires have shown that these events can lead to dramatic negative health impacts. For example, the 1997/1998 Indonesian fire event led to an extreme smoke haze event causing severe deleterious human health effects (Kunii et al., 2002). Another peat fire in 2008 occurred in eastern North Carolina over a period of several months, producing a large regional smoke haze pollution event. Rappold et al. (2011) found that this peat fire event led to significant increases in emergency department visits for respiratory and cardiovascular health problems. Furthermore, Kim et al. (2014) has demonstrated that exposure of ambient PM sampled from this 2008 peat wildfire event resulted in significant pulmonary and cardiovascular effects in mice.

Biomass burning smoke has been shown to contain a substantial number of hazardous gas- and particle-phase compounds including monoaromatic VOCs, aldehydes, 1,3-butadiene, polycyclic aromatic hydrocarbons, and chlorinated organics (Naeher et al., 2007). Currently, the research devoted to quantifying emission factors for these hazardous pollutants from peat fires is sparse. However, air quality models require accurate emission factor data for speciated gas and particulate pollutants, particularly those on the U.S. EPA list of hazardous air pollutants (HAPs) (US EPA, 2005), to predict the impact of peat fires on air quality and human health. Detailed speciation of smoke PM also allows for more accurate source apportionment of PM.

The objective of this work is to quantify gas and particulate emission factors for temperate peat fires. Small-scale laboratory burn experiments were conducted with peat samples from North Carolina, U.S., to determine emission factors for a range of trace gas and particulate species. Emission factors for criteria pollutants (i.e. CO₂, CO, total hydrocarbons, NO_x), fine particulate matter (PM_{2.5}) mass, elemental carbon (EC), organic carbon (OC) and semivolatile components will be reported in a companion paper (Black et al., 2016). This paper focuses on the chemical characterization of PM_{2.5} and speciated VOC emissions, with an emphasis on hazardous air pollutants resulting from peat burning.

2. Materials and methods

A detailed description of the experimental methods for the peat sample collection and peat burning experiments used in this study have been provided in a companion paper (Black et al., 2016). Here, a brief summary of general experimental procedures is given along with a detailed account of analytical procedures followed for the speciated gas- and particle-phase organic compounds.

2.1. Peat sampling

Peat core samples were taken from two wildlife refuge sites located on the coastal plains of Eastern North Carolina, U.S.: Alligator River National Wildlife Refuge (AR peat) and Pocosin Lakes National Wildlife Refuge (PL peat). Further information regarding prevailing vegetation types at these wetland sites has been provided elsewhere (Geron and Hays, 2013). Peat core samples of 15 cm diameter and 20–25 cm depth were taken from each site. The peat samples were dried in an oven for 24 h at 100 °C and stored intact until used. The carbon content for the two samples was 30% and 28%, and chlorine content was 187 ppm and 455 ppm for PL and AR samples, respectively. Chemical analyses of the peat samples are discussed in greater detail elsewhere (Black et al., 2016).

2.2. Laboratory burning experiment

Peat core samples were burned in U.S. Environmental Protection Agency's Open Burn Test Facility (OBTF) at the Research Triangle Park, NC, location described in detail elsewhere (Black et al., 2011). A high volume fan facilitated the introduction of ambient air into the OBTF chamber at a volume exchange time of ~90 s to maintain oxygen levels representative of open burning. Each burn experiment was initiated by placing a peat core (1.5–2.5 kg mass) housed inside a stove pipe on a top pan balance and briefly igniting the top center surface by propane torch. Continuous emissions sampling of CO₂, CO, O₂ and total hydrocarbons (THC) and time-integrated sampling of VOCs, and PM_{2.5} commenced approximately one minute after fire ignition. The fires were characterized by a brief flaming phase followed by an extended period of smoldering. Smoke sampling of the peat burns continued for approximately 5–7 h. Laboratory burns were carried out in triplicate for both of the two peat sample sites (Pocosin Lakes and Alligator River).

2.3. Sampling procedures

A detailed description of the sampling methods for the CEM measurements can be found in Black et al. (2016). The following outlines the sampling procedure for VOC, carbonyl and PM_{2.5} sampling. Smoke emissions were sampled through a heated line (~110 °C) with the inlet placed above the sample inside a metal hood. The sampling line was split to a SUMMA canister and a 2,5-dinitrophenylhydrazine (DNPH)-coated cartridge (Sigma-Aldrich Corp., St. Louis, MO, U.S.) for quantification of VOCs and carbonyls, respectively. A quartz filter (Pall Corp., Port Washington, NY, U.S.) was placed before the canister/cartridge sampling trains to reduce PM contamination of samples. Time-integrated canister and DNPH cartridge samples were taken each hour. A custom-made fitting with a critical orifice controlled sampling flow rate (~70 standard cm³ min⁻¹) to a pre-cleaned and evacuated SUMMA canister. Canisters were filled to below ambient pressure, typically to ~0.6 atm, during one hour of sampling time. The flow through the

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