



Preliminary assessment of the anthropogenic and biogenic contributions to secondary organic aerosols at two industrial cities in the upper Midwest



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H I G H L I G H T S

- Anthropogenic and biogenic SOC quantified at urban and rural locations.
- Anthropogenic SOC contributed significantly during summer months.
- SOA may be partially controllable by reduction of anthropogenic VOC emissions.

A R T I C L E I N F O

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The contributions of anthropogenic and biogenic secondary organic carbon (SOC) to total PM_{2.5} mass are of interest to air quality management agencies required to demonstrate maintenance of the PM_{2.5} NAAQS. Reductions of SOC can be used in conjunction with the mitigation of other PM_{2.5} constituents to maintain PM_{2.5} concentrations below the regulatory limit. Currently, quantitative tools to understand the SOC source contributions to PM_{2.5} mass are not well developed, and the spatial variation of different types of SOC is not known.

In this study concentrations of anthropogenic and biogenic SOC mass were determined using PM_{2.5} measurements made in Cleveland, OH and Mingo Junction, OH. Twenty-four hour averaged samples were collected on the EPA 1-in-6 day schedule over the course of one year between June 2007 and May of 2008. Organic molecular markers for anthropogenic and biogenic SOC were extracted from the PM_{2.5}, silylated, and then analyzed by GC–MS. Source apportionment calculations were conducted using the EPA CMB (v.8.2) software and organic molecular markers as source tracers.

SOC concentrations calculated from SOC tracers measurements followed the expected seasonal patterns with maximum contributions during the summer and minimum contributions during the winter. Anthropogenic SOC constituted approximately 37% to the apportioned SOC and 6% to the measured OC, on average across both sites. Biogenic SOC contributed the 42% to the apportioned SOC, and 4% to the measured OC. Anthropogenic SOC contributed strongly to organic PM_{2.5} meaning that SOC may be partially controllable by reductions in VOC emissions from anthropogenic sources.

Similarities in the month-to-month patterns in α -pinene markers were observed between Cleveland and Mingo Junction, suggesting a regional character to this type of SOC. However, such patterns were not readily apparent in the isoprene markers.

Limitations were found in the current version of the model. Approximately half of the water soluble organic carbon unrelated to biomass burning (NB-WSOC) during spring, summer and early fall could not be apportioned by the CMB model with the SOC markers available during this study. This suggested that additional sources not included in the CMB model used in this study contributed to SOC, or that models using markers measured in chamber oxidations are not entirely representative of the study sites. The unapportioned OC did not correlate particularly well with any of the known OC sources. While

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performance of the model is limited due to uncertainties in the source profiles, the apportionments calculated still give a preliminary insight into the relative contributions to SOC from anthropogenic and biogenic emissions.

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1. Introduction

Respirable particulate matter (PM) is associated with increased mortality and morbidity (Pope and Dockery (2006)), and as a result has been regulated in many developed countries. Secondary organic aerosols (SOA) contribute to respirable PM and some health studies have suggested a direct link between SOA and adverse health effects (Mills et al. (2009); Brook et al. (2010); Delfino et al. (2010)). SOA are predominantly formed from oxidation of biogenic VOC emissions in locations not impacted heavily by anthropogenic emissions of VOCs, (Heald et al. 2006, Kirillova et al. 2010, Gilardoni et al. 2011), while SOC formed from the oxidation of anthropogenic VOCs contributes significantly in urban environments (Lewandowski et al. 2008; Stone et al. 2009). Anthropogenic SOC is likely to be easier to mitigate than biogenic SOC, so understanding the relative contributions from these sources will be helpful from an air quality management perspective.

Trees, plants, and grasses emit a wide variety of VOCs which range in reactivity to atmospheric oxidants. Isoprene, α -pinene, and β -caryophyllene are considered to be the most important biogenic VOCs from the perspective of SOA formation and therefore are the focus BVOCs of this study. Motor vehicles and industrial processes emit a complex mixture of VOCs which range in composition between alkane, alkenes, to single and multiple ring aromatics which may also be functionalized with side chains. Toluene is only released by anthropogenic activities in most locations, and is considered to contribute significantly to SOA. Furthermore, toluene is thought to share oxidation products with *m*-xylene, and therefore may be representative of a wider range of single ring aromatics (Kleindienst et al. (2007)).

SOA constitute a significant fraction of $PM_{2.5}$ mass but the exact contributions remain uncertain. Recent publications report as much as 85% of organic matter (OM) (Gilardoni et al. (2011); Po Valley, Italy) and 88% of water soluble OC (WSOC) can be due to SOC during summer (Kirillova et al. (2010); Stockholm, Sweden). Uncertainty also exists regarding the relative contributions between biogenic and anthropogenic sources to SOA and whether all sources of SOA have been accounted for. Stone et al. (2009) demonstrated that in Cleveland, OH and Detroit, MI anthropogenic SOA could contribute much greater than half of the SOC observed in weekend and weekday composites collected during the summer. The same study also revealed that a much greater percentage of the secondary organic carbon could be identified in the upper Midwest than at Riverside, CA, (in the Los Angeles air basin). Despite this, the sources of about 20% of OC remained unidentified on average in Cleveland and Detroit.

The purpose of this study is to characterize the contributions of biogenic and anthropogenic SOC to total PM OC over the course of one year at Cleveland, OH and Mingo Junction, OH. A Chemical Mass Balance model employing published source profiles is used to apportion OC in monthly composites of 24 h averaged samples collected on the EPA 1-in-6 day schedule during 2007 and 2008.

2. Methods

2.1. Sample collection locations

Daily average particulate matter smaller than $2.5 \mu\text{m}$ in aerodynamic diameter ($PM_{2.5}$) was collected at Cleveland, OH and

Mingo Junction, OH on the EPA 1-in-6 day schedule. The sampler at Cleveland was located next to the Cuyahoga River Valley, on a cabin next to a surface street intersection at E 14th St and Orange Ave (41.49396°N ; -81.67850°W). The site was next to the interchange between I-77 and I-90, and was immediately adjacent to the heavy industry in the river valley. Cleveland, OH, has a large district of heavy industry along the Cuyahoga River that runs through Cleveland and into Lake Erie in downtown Cleveland. The site was also close to a major interchange between freeways that connect the suburbs with the downtown business district.

The sample collection site at Mingo Junction was located on the roof of the emergency services headquarters (40.32194°N ; -80.6064°W) which was on the opposite side of the Ohio River Valley to a steel mill which ran the length of the small community. It was situated a few miles from Steubenville, OH, the city with the highest PM associated mortality in the Harvard Six Cities study (Dockery et al. (1993)). There are many other large coal burning industrial facilities along the Ohio River Valley near Mingo Junction.

2.2. Collections of atmospheric particulate matter

$PM_{2.5}$ was collected using URG 3000B aerosol samplers operated at 92 LPM (URG Corp, Chapel Hill, NC). UW-Madison samplers were collocated with the US EPA Chemical Speciation Network (CSN) samplers at each monitoring site and operated by local agencies.

Clean handling techniques were employed to avoid contamination of the samples. The internal surfaces of the UW-Madison PM samplers were coated in high-density Teflon. These surfaces and the stainless steel tweezers used to handle the filter substrates were cleaned by washing with warm water and Neutrad soap (Decon Laboratories, King of Prussia, PA), and rinses with deionized water ($18.2 \text{ M}\Omega$ resistance), hexane, and acetone in that order. The $PM_{2.5}$ was collected on 90 mm quartz fiber filters pre-cleaned by baking at 550°C for 15 h, and sealed in foil-lined Petri dishes. Filter substrates were handled using ultra clean techniques (Sheesley et al. 2004; Lough et al. 2007). The substrates were stored at -20°C , and shipped frozen to the laboratory (Stone et al. (2008)).

2.3. Organic carbon and elemental carbon measurements

Total organic carbon measurements (Schauer et al (2003)) provided a total mass of OC to be allocated to the various source categories included in a source apportionment model. Total elemental carbon measurements were used as a marker species. Filter sections measuring 1.5 cm^2 in area were excised from 24 h averaged samples collected on the EPA 1-in-6 day schedule samples using quartz filters. OC and EC analyses were conducted with an OC-EC analyzer (Sunset Laboratories, Tigard, OR) using the ACE-ASIA method (Schauer et al (2003)). Blank corrections were performed using field blank filters that were loaded and immediately removed from the filter holders in order to represent the contamination associated with storage, transport, and handling. Field blank values were approximately $0.2 \mu\text{g m}^{-3}$ for OC and negligible for EC.

2.4. Aluminum and silicon measurements

Aluminum and silicon concentrations in $PM_{2.5}$ were downloaded from the CSN database USEPA (2008).

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