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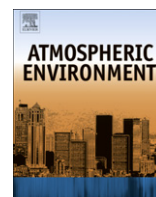
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Temperature response of the submicron organic aerosol from temperate forests

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ABSTRACT

Observations from four periods (three late springs and one early summer) at temperate forest sites in western and eastern Canada offer the first estimation of how the concentrations of submicron forest organic aerosol mass (SFOM) from the oxidation of biogenic volatile organic compounds (BVOC) vary over the ambient temperature range of 7 °C to 34 °C. For the measurement conditions of clear skies, low oxides of nitrogen and within approximately one day of emissions, 50 estimates of SFOM concentrations show the concentrations increase exponentially with temperature. The model that is commonly used to define terpene emissions as a function of temperature is able to constrain the range of the SFOM values across the temperature range. The agreement of the observations and model is improved through the application of an increased yield of SFOM as the organic mass concentration increases with temperature that is based on results from chamber studies. The large range of SFOM concentrations at higher temperatures leaves open a number of questions, including the relative contributions of changing yield and of isoprene, that may be addressed by more ambient observations at higher temperatures.

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1. Introduction

The responses of biota to global change are important sources of uncertainty for climate prediction (e.g. Andreae and Crutzen, 1997) and air quality regulation (e.g. Carlton et al., 2009). Forests emit isoprene and terpene compounds, collectively denoted here as “biogenic volatile organic compounds” (BVOCs), at a rate dependent on ambient temperature and photosynthetic light (e.g. Guenther et al., 2006); oxygenated emissions are excluded from the BVOC definition for this discussion. Once in the atmosphere, the BVOCs can be rapidly oxidized leading to an increase in the fine particle (<1 µm diameter) organic mass concentration or submicron forest organic mass (SFOM) that gives rise to the bluish haze often observed in forested mountain valleys (Went, 1960).

Global emissions of BVOCs are estimated to be an order of magnitude higher than anthropogenic VOCs (e.g. Goldstein and Galbally, 2007). Terpenes, considered the main BVOC precursors of SFOM, have been linked to increases in ambient aerosol number concentrations (e.g. Tunved et al., 2006; Slowik et al., 2010), and their global direct atmospheric cooling potential has been estimated at 0.04–0.24 W m^{−2} (Carslaw et al., 2010) with potentially greater cooling from effects on clouds (Spracklen et al., 2008). Isoprene may also contribute to SFOM (Claeys et al., 2004; Kroll et al., 2005) or possibly inhibit its formation (Kiendler-Scharr et al., 2009). Global isoprene emissions are about five times those of terpenes (Fowler et al., 2009), but the yields of OM from isoprene oxidation are much lower than from terpene oxidation (e.g. Carlton et al., 2009). Yields of fine particle organic mass (OM) from BVOC oxidation are reduced at higher temperatures due to increased volatilization (e.g. Chan et al., 2009) but they can be enhanced by increased OM levels due to mass absorption (Pankow, 1994). For example, the global burden of OM is predicted to increase by 2100 (Tsigaridis and Kanakidou, 2007) and mass absorption due to the

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anticipated increase in future anthropogenic OM is expected to enhance the SFOM (Heald et al., 2008).

Forests cover about 45% of the surface area of Canada (<http://cfs.nrcan.gc.ca>) and there are many places to study the SFOM free of significant anthropogenic influence. Observations of OM within and downwind of forests in eastern and western Canada during the late springs of 2006–2008 and the early summer of 2009 are used to estimate the concentrations of SFOM at temperatures ranging from 7–34 °C; the late spring and early summer are the optimal periods for terpene production at the latitudes of these observations (Schurgers et al., 2009). The variation of the SFOM mass concentrations with temperature is compared with simulated variations of SFOM based on empirical formulations of BVOC emissions with temperature. These results offer new context for examining the hypothesis that SFOM concentrations can be effectively simulated in models based on terpene emissions rates as a function of temperature.

2. Methods

The 2006, 2008 and 2009 observations were made at Whistler, British Columbia (50.1° N, 122.9° W). Whistler Village (675 m-MSL) is in a valley about 120 km northeast of Vancouver and trees line the valleys in the region up to about 1850 m. The 2006 observations (Leaitch et al., 2009) are taken from aircraft profiles at Whistler, the 2008 measurements (Schwartz et al., 2010) were made at 1019 m on Whistler Mountain immersed in the biogenic source region, and the 2009 measurements (Takahama et al., 2010) were collected at the peak of Whistler Mountain (2182 m) that is frequently immersed in the valley air during the spring to fall (Gallagher et al., in press). About 90% of the trees in the Whistler region are

coniferous species. The 2007 observations were made at Egbert, Ontario (44.2° N, –79.8° W; 253 m), which is in a rural area about 75 km northwest of Toronto. The periods of predominantly SFOM at Egbert occurred during episodes of air arriving from over forests to the north within approximately one day travel time (Vlasenko et al., 2009; Slowik et al., 2010). Those forests are approximately an equal mix of coniferous and broadleaf species (<http://cfs.nrcan.gc.ca>).

2.1. Instrumentation

Table 1 summarizes the instrumentation most relevant to this work used in each of the four studies. The details of sampling techniques, calibrations and processing of data are described in the above references. During 2006, OM was measured with an Aerodyne Quadrupole Aerosol Mass Spectrometer (Q-AMS; Jayne et al., 2000) deployed on a Cessna 207 aircraft. During 2007, the OM concentrations were measured using an Aerodyne C-Time-of-Flight Aerosol Mass Spectrometer (C-AMS) and VOCs were measured with a Proton-Transfer Reaction Mass Spectrometer (PTR-MS; Lindinger et al., 1998). During 2008, the OM are taken from a High Resolution Time-of-Flight AMS (HR-AMS; Drewnick et al., 2005) and adjusted to the OM obtained from the organic functional group (OFG) concentrations of submicron particles collected over 12 h on Teflon filter samples and analyzed by Fourier Transform Infrared Spectroscopy (FTIR) using the approach of Russell (2003). VOCs were measured with a PTR-MS. During 2009, half-hour averaged mass concentrations of sulphate, nitrate and total organics at <1 µm diameter were measured with an Aerodyne Aerosol Chemical Speciation Monitor (ACSM; Ng et al., 2011) and compared with 1–4 day integrated filter samples also analyzed by FTIR as above.

Table 1
Measurement techniques.

| Project; platform; references | Measurement | Technique | Detection Limits (3σ) |
|--|---|--|---|
| Whistler 2006 Cessna aircraft; Leaitch et al. (2009) | OM, sulphate and nitrate mass concentrations; particles <1 µm vacuum aerodynamic diameter (VAD). | Aerodyne Quadrupole Aerosol Mass Spectrometer (2 min averages) | Sulphate – 40 ng m ⁻³ ; Nitrate – 40 ng m ⁻³ ; Organics – 600 ng m ⁻³ . |
| | Particle size distribution (120–700 nm diameter) | PMS PCASP-100X | |
| Egbert 2007 Ground-based at 253 m-MSL; Vlasenko et al. (2009); Slowik et al. (2010). | OM, sulphate and nitrate mass concentrations; particles <1 µm VAD | Aerodyne C-ToF-AMS (30 min.) | Sulphate – 0.5 ng m ⁻³ ; Nitrate – 0.5 ng m ⁻³ ; Organics – 10 ng m ⁻³ . |
| | Particle size distributions Volatile Organic Compounds (VOCs) | TSI-Scanning Mobility Particle System (SMPS) Proton-Transfer Reaction Mass Spectrometer | Toluene – 43 pptv; Isoprene – 104 pptv; Monoterpenes – 180 pptv. |
| Whistler 2008 Ground-based at 1019 m-MSL; Schwartz et al. (2010). | OM concentrations | Analysis of filter by FTIR for organic mass concentrations (12 h) | <0.2 µg m ⁻³ |
| | OM/sulphate | Aerodyne V-ToF-AMS (30 min.) | Detection limits: Sulphate – 1 ng m ⁻³ ; Nitrate – 1 ng m ⁻³ ; Organics – 10 ng m ⁻³ . |
| | Particle size distributions VOCs | TSI-Scanning Mobility Particle System (SMPS) Proton-Transfer Reaction Mass Spectrometer | Toluene – 43 pptv; Isoprene – 104 pptv; Monoterpenes – 180 pptv. |
| Whistler 2009 Ground-based at 2182 m-MSL; Takahama et al. (2010) | OM concentrations | Analysis of filter by FTIR for organic mass concentrations (3 days) | <0.1 µg m ⁻³ |
| | OM, sulphate and nitrate mass concentrations; particles <1 µm VAD | Aerodyne ACSM (30 min averages) | Detection limits: Sulphate – 40 ng m ⁻³ ; Nitrate – 40 ng m ⁻³ ; Organics – 600 ng m ⁻³ . |
| | Particle size distributions | TSI-Scanning Mobility Particle System (SMPS) | |

Particle concentrations may be reduced in the AMS and ACSM due to oven collection and inlet transmission efficiencies less than unity (e.g. Liu et al., 2007; Matthew et al., 2008). In 2006, the mean collection efficiency was found to be close to unity based on a number of comparisons (Leitch et al., 2009), but the OM could be underestimated here as transmission losses were only partly addressed. For 2007, Slowik et al. (2010) used comparison with size distributions and individual particle light scattering within the C-AMS to arrive at a mean collection efficiency of 0.6, and a factor of 1.67 has been applied to the data used here. The transmission of larger submicron particles (0.6–1 μm) was not considered and therefore the OM may be slightly underestimated. The 2008 HR-AMS data have been adjusted by a constant 1.6 factor, based on a comparison with the <1 μm filter FTIR OM (Schwartz et al., 2010). As for 2008, the 2009 mass concentrations from the ACSM were scaled for a mean factor of 1.75 based on the comparison with OM concentrations measured by FTIR (Takahama et al., 2010). The adjustments to the 2008 and 2009 for the filter OM account for collection and transmission deficiencies in the AMS and ACSM. The overall uncertainty, based on the comparisons with the filter OM measurements by the FTIR (approximately $\pm 21\%$; Russell, 2003) and with other particle measurements ($\pm 25\%$; Leitch et al., 2009; Slowik et al., 2010), is $\pm 25\%$.

2.2. SFOM and temperature classification

Four common criteria are used to delineate the SFOM from the OM measurements for each of the four studies:

- 1) The afternoon skies were free of visible cloud. For the studies discussed here, the latitudes of the BVOC sources are similar for all cases and the observations were made within approximately four weeks either side of the summer solstice. The no-cloud constraint minimizes potential bias in the SFOM due to changes in photosynthetic and actinic radiation.
- 2) Local wind speeds $\geq 1 \text{ m s}^{-1}$. The wind speed criterion is imposed to reduce possible accumulation due to stagnating air as discussed in section 3.
- 3) Only periods with the mass weighted submicron fraction $\text{OM}/(\text{OM} + \text{sulphate}) > 0.7$ are used to minimize anthropogenic contributions as indicated by the sulphate aerosol; the mean fraction of the final selected SFOM is 0.85.
- 4) The selected SFOM selected are one-hour averaged mass concentrations near the time of the daytime maximum temperature (approximately 1700 local time) and near the times of the minimum temperature (ca. 0600 LT).

Criteria used to delineate the SFOM from the OM that are specific to a study are described in sections 2.2.1–2.2.4.

Some portion of the OM in the selected points may be of anthropogenic origin and all OM concentrations are reduced to account for this anthropogenic factor based on the sulphate associated with the selected OM. The OM anthropogenic factor is taken as the mean value of the mass concentration weighted ratio of OM to sulphate obtained from anthropogenic measurements during the 2007 study; the 2007 study is used because it had the largest influence from anthropogenic sources. The SFOM values are then defined as

$$\text{SFOM} = \text{OM} - ((\text{OM}/\text{SO}_4)_{\text{anthropogenic mean}} * \text{SO}_4) \quad (1)$$

where SO_4 is the sulphate mass concentration corresponding to the selected OM. The value of $(\text{OM}/\text{SO}_4)_{\text{anthropogenic mean}}$ applied to the present four studies is 1.52, which is larger than the mean of a number of Northern Hemisphere measurements (0.93) from

Zhang et al. (2007). The result using 0.93 in place of 1.52 is discussed in section 3.1.

There are three factors considered for the selection of temperature:

- 1) Local temperature – For each daytime SFOM data point, the maximum daytime one-hour temperature is used. In the case of the nighttime SFOM data points, the previous day's maximum temperature is used.
- 2) Regional temperature – For most situations when the OM was dominated by biogenic sources, the winds were relatively light and the local temperature is a reasonable measure of the regional temperature. In the case of Egbert 2007, as discussed below, slightly higher temperatures were observed upwind of the measurements and those temperatures are used to represent the emissions region.
- 3) Vertical distribution at Whistler – The majority of the forest resides on the slopes of the mountains in the region rather than on the valley floor, extending from approximately 650 m to 1850 m. Temperatures are taken from 933 m, approximately one-quarter up the slope between the valley and the tree line, for all three Whistler studies. Assuming that the terpene emissions follow the commonly used function of temperature (equation (2)), an adiabatic lapse rate and a constant tree number with altitude, then approximately 35% of the emissions are estimated to occur below the 933 m level. Reductions in tree density per unit area with elevation and changes in land area with the mountain slope will likely increase the estimate of the percentage of emissions below 933 m, and hence the 933 m temperatures are reasonable estimates of the mean influence of the vertical distribution of temperature on the BVOC emissions.

2.2.1. Egbert 2007

Further to the above common criteria for SFOM, the 2007 one-hour OM points are discriminated to include only northerly wind directions because the influence of anthropogenic sources is substantially reduced for air from the north (e.g. Chan et al., 2010; Liggio et al., 2010; Slowik et al., 2010) and the forest density increases to the north.

The 2007 time series of the OM, sulphate aerosol mass concentrations, the SFOM periods and periods of winds from the north are shown in Fig. 1. The selected SFOM periods were further considered relative to the analyses of Vlasenko et al. (2009) and Slowik et al. (2010) who used Positive Matrix Factorization (PMF) applied to anthropogenic VOCs, BVOCs (terpenes and isoprene) and aerosol chemical components to identify components of observation periods associated with biogenic, anthropogenic and biomass burning sources. Twelve OM points from the 2007 study are considered here as predominantly biogenic in origin, eight of which are from the 5-day biogenic case study that was a focus of Slowik et al. (2010). The other four points come from earlier in the study and correspond with reduced concentrations of anthropogenic and biomass burning markers (acetylene, potassium and acetonitrile) and increased concentrations of monoterpenes. During the case study, the daytime temperatures to the north were uncommonly as much as 4 °C higher than at Egbert. The maximum temperatures from that region are used here; specifically the temperatures at Muskoka, Ontario (45.0° N, 79.3° W) were selected because trajectories suggest an air parcel transit time of 12–24 h from near Muskoka.

A summary of the SFOM concentrations and temperatures is given in Table 2 for the daytime points and Table 3 for the nighttime points. The tables also give the corresponding mixing ratios of ozone and NO_x where available. For the Egbert 2007 study, the NO_x

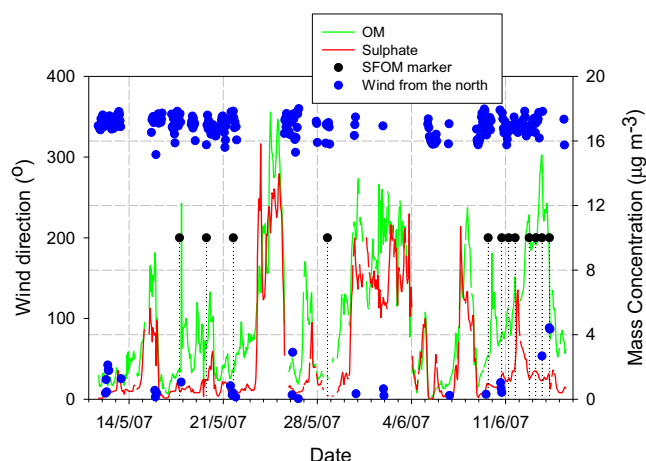


Fig. 1. Time series from the Egbert 2007 study of the OM and sulphate mass concentrations, the periods when the OM is defined as SFOM (12 points identified with black dots) and the periods when the wind direction was from the north (blue dots).

levels are $<1.1 \text{ nmol mol}^{-1}$ for the daytime cases (mean of $0.67 \text{ nmol mol}^{-1}$). Higher NO_x values during the nighttime are due to trapping of local emissions within the boundary layer. The ozone levels are reduced during the nighttime because of titration by the increased NO_x and deposition within the nocturnal boundary layer.

2.2.2. Whistler 2008

Time series of OM and sulphate mass concentrations as well as ambient temperatures for the Whistler 2008 study are shown in Fig. 2. The black dots with dropped lines represent the complete

filter OM concentration dataset (51 points) based on the OFG analyses. The 20 black dots with yellow centres are the selected SFOM periods. The selected SFOM are one-hour averaged values from the HR-AMS corresponding to approximately 0600 and 1700 local times (PST) during the selected period.

The wind direction is not used for definition because Whistler is immersed in the source region and there are no local anthropogenic sources of sufficient scale to impact the regional OM. Further, for the periods selected here, trajectory analysis does not show the air to have arrived from the Vancouver area, the nearest large urban centre (Schwartz et al., 2010).

The selected SFOM points correspond with the submicron OM dominated by biogenic components as given by Schwartz et al. (2010) who applied PMF to the OFG measurements and used correlations with monoterpenes and the biogenic oxidation products methyl-vinylketone and methacrolein to identify biogenic and combustion factors contributing to the mass concentrations of the submicron aerosol. Further identification of SFOM was done through comparison of the OFG with OM products of BVOC oxidation measured in chamber studies.

The SFOM values for 2008 are also given in Tables 2 and 3. The ozone values at this mid-mountain site were lower than those from the Egbert site by $10\text{--}20 \text{ nmol mol}^{-1}$. In contrast to the Egbert 2007 observations, the mean NO_x values at the Whistler 2008 site are much lower at night than during the day. During the nighttime, the site was above the nocturnal boundary layer and there were no nearby local sources. During the daytime, the site was occasionally influenced by passing trucks. These emissions affected the NO_x measurements, but they do not reflect the regional NO_x levels nor did they significantly impact the OM mass concentrations (Schwartz et al., 2010). The nighttime NO_x values are more representative of the regional NO_x levels.

Table 2

Summary of daytime observations.

| Project | Max. temp. ($^{\circ}\text{C}$) | RH (%) | OM ($\mu\text{g m}^{-3}$) | Sulphate ($\mu\text{g m}^{-3}$) | SFOM ($\mu\text{g m}^{-3}$) | OM/(OM + SO_4) % | Ozone (nmol mol^{-1}) | NO_x (nmol mol^{-1}) |
|----------------------|-----------------------------------|--------|-----------------------------|-----------------------------------|-------------------------------|----------------------------|----------------------------------|--|
| <i>Whistler 2009</i> | | | | | | | | |
| 20/07/2009 17:17 | 27.5 | 33 | 2.64 | 0.36 | 2.10 | 88 | 33 | |
| 21/07/2009 17:46 | 29.8 | 28 | 3.56 | 0.60 | 2.65 | 86 | 49 | |
| 24/07/2009 17:07 | 24.3 | 57 | 4.13 | 0.48 | 3.41 | 90 | 30 | |
| 25/07/2009 17:42 | 28.3 | 60 | 3.83 | 0.44 | 3.16 | 90 | 24 | |
| 26/07/2009 17:42 | 30.1 | 54 | 4.92 | 0.26 | 4.53 | 95 | 24 | |
| 27/07/2009 17:42 | 34.2 | 37 | 4.75 | 0.26 | 4.31 | 94 | 26 | |
| 28/08/2009 17:42 | 26 | 38 | 2.54 | 0.42 | 1.90 | 86 | 48 | |
| <i>Egbert 2007</i> | | | | | | | | |
| 17/05/2007 17:45 | 15.6 ^a | 48 | 1.88 | 0.59 | 0.99 | 76 | 49 | 0.5 |
| 19/05/2007 17:34 | 21.5 ^a | 30 | 3.13 | 1.19 | 1.32 | 72 | 72 | 0.5 |
| 21/05/2007 18:05 | 16.7 ^a | 36 | 1.67 | 0.50 | 0.91 | 77 | 46 | 0.6 |
| 28/05/2007 17:25 | 16 ^a | 60 | 1.44 | 0.21 | 1.13 | 87 | 38 | 0.6 |
| 09/06/2007 17:13 | 21.5 ^a | 41 | 2.74 | 0.88 | 1.40 | 76 | 47 | 0.5 |
| 10/06/2007 17:25 | 24 ^a | 41 | 4.15 | 1.52 | 1.83 | 73 | 58 | 0.5 |
| 11/06/2007 16:40 | 28.7 ^a | 48 | 7.58 | 2.07 | 4.44 | 79 | 55 | 1.1 |
| 12/06/2007 17:45 | 31.2 ^a | 43 | 11.41 | 1.32 | 9.40 | 90 | 53 | 0.9 |
| 13/06/2007 16:46 | 32.1 ^a | 45 | 15.13 | 1.15 | 13.4 | 93 | 56 | 1.0 |
| <i>Whistler 2008</i> | | | | | | | | |
| 21/05/2008 16:40 | 12.1 | 71 | 0.60 | 0.12 | 0.42 | 76 | 31 | 1.4 |
| 22/05/2008 16:40 | 15.4 | 64 | 1.03 | 0.11 | 0.86 | 90 | 24 | 4.1 |
| 23/05/2008 16:40 | 16.1 | 47 | 1.11 | 0.21 | 0.79 | 79 | 30 | 1.5 |
| 24/05/2008 16:40 | 20.2 | 42 | 1.36 | 0.22 | 1.03 | 81 | 37 | 0.5 |
| 25/05/2008 15:30 | 20.8 | 54 | 1.19 | 0.18 | 0.92 | 92 | 36 | 0.6 |
| 27/05/2008 16:30 | 15.5 | 73 | 1.52 | 0.27 | 1.11 | 88 | 31 | 1.4 |
| 28/05/2008 16:00 | 17.5 | 68 | 1.58 | 0.33 | 1.08 | 86 | 33 | 1.8 |
| 14/06/2008 16:40 | 15.2 | 55 | 1.26 | 0.32 | 0.77 | 77 | 31 | 0.9 |
| 15/06/2008 16:00 | 17.9 | 50 | 1.54 | 0.34 | 1.02 | 82 | 31 | 0.5 |
| <i>Whistler 2006</i> | | | | | | | | |
| 16/05/2006 17:00 | 25.8 | 46 | 4.31 | 0.58 | 3.43 | 88 | 51 | |

^a Previous day Muskoka.

Table 3
Summary of nighttime observations.

| Project | Temp. (°C) | RH (%) | Prior day max. temp. (°C) | OM ($\mu\text{g m}^{-3}$) | Sulphate ($\mu\text{g m}^{-3}$) | SFOM ($\mu\text{g m}^{-3}$) | OM/ (OM + SO ₄) % | Ozone (nmol mol ⁻¹) | NO _x (nmol mol ⁻¹) |
|----------------------|-------------------|-----------|------------------------------|--------------------------------|--------------------------------------|----------------------------------|----------------------------------|------------------------------------|--|
| <i>Whistler 2009</i> | | | | | | | | | |
| 22/07/2009 5:29 | 15.3 | 62 | 29.8 | 3.43 | 0.41 | 2.80 | 89 | 33 | |
| 23/07/2009 5:37 | 13.1 | 86 | 27.5 | 3.64 | 0.63 | 2.67 | 85 | 31 | |
| 24/07/2009 5:37 | 13 | 96 | 23 | 2.86 | 0.58 | 1.99 | 83 | 29 | |
| 25/07/2009 5:15 | 14.3 | 66 | 24.3 | 2.54 | 0.34 | 2.02 | 88 | 19 | |
| 26/07/2009 5:42 | 15.5 | 73 | 28.3 | 3.47 | 0.30 | 3.02 | 92 | 22 | |
| 27/07/2009 5:42 | 18.9 | 63 | 30.1 | 4.25 | ≤0.04 | 4.25 | 99 | 27 | |
| 28/08/2009 5:42 | 15.1 | 29 | 28.3 | 2.11 | 0.46 | 1.41 | 82 | 51 | |
| 13/09/2009 6:25 | 14.6 | 40 | 27.7 | 3.15 | 0.09 | 3.01 | 97 | 45 | |
| <i>Egbert 2007</i> | | | | | | | | | |
| 11/06/2007 5:30 | 4.6 ^a | 91 | 24 ^a | 5.07 | 1.35 | 3.03 | 79 | 32 | 2.0 |
| 13/06/2007 5:50 | 14 ^a | 76 | 31.2 ^a | 9.61 | 1.75 | 6.96 | 85 | 42 | 1.2 |
| 14/06/2007 5:56 | 14.1 ^a | 86 | 32.1 ^a | 8.14 | 1.34 | 6.10 | 86 | 42 | 2.6 |
| <i>Whistler 2008</i> | | | | | | | | | |
| 17/05/2008 06:00 | 10.5 | 60 | 18.7 | 1.24 | 0.26 | 0.84 | 91 | 36 | 0.2 |
| 21/05/2008 05:40 | 2.9 | 90 | 7.5 | 0.48 | 0.14 | 0.27 | 77 | 29 | 0.4 |
| 21/05/2008 05:40 | 5 | 90 | 12.1 | 0.57 | 0.12 | 0.39 | 73 | 17 | 0.3 |
| 23/05/2008 05:40 | 9 | 60 | 15.4 | 0.94 | 0.27 | 0.53 | 83 | 29 | 0.2 |
| 24/05/2008 05:40 | 11.8 | 59 | 16.1 | 0.87 | 0.15 | 0.64 | 85 | 29 | 0.2 |
| 25/05/2008 05:50 | 13.2 | 61 | 20.2 | 1.40 | 0.20 | 1.10 | 91 | 31 | 0.1 |
| 26/05/2008 05:50 | 8.1 | 91 | 20.8 | 1.03 | 0.11 | 0.86 | 91 | 24 | 0.2 |
| 31/05/2008 06:00 | 4.6 | 84 | 14.9 | 1.37 | 0.17 | 1.11 | 91 | 25 | 0.6 |
| 14/06/2008 06:00 | 3.7 | 85 | 12.5 | 1.16 | 0.33 | 0.66 | 81 | 22 | 0.2 |
| 15/06/2008 06:00 | 4.4 | 85 | 15.2 | 1.59 | 0.34 | 1.07 | 76 | 19 | 0.5 |
| 16/06/2008 06:00 | 5.6 | 85 | 17.9 | 1.84 | 0.28 | 1.41 | 82 | 19 | 0.2 |
| <i>Whistler 2006</i> | | | | | | | | | |
| 16/05/2006 10:00 | 19.9 | | 24.4 | 2.91 | 0.69 | 1.86 | 81 | 52 | |
| 17/05/2006 10:00 | 18.2 | | 25.8 | 4.78 | 0.57 | 3.92 | 89 | 51 | |

^a Muskoka.

2.2.3. Whistler 2009

The time series of half-hour averaged OM and sulphate mass concentrations and wind speeds from the Peak of Whistler Mountain in the summer of 2009 are shown in Fig. 3. The one-hour SFOM points are indicated by the vertical markers for the periods of maximum daytime temperature and minimum nighttime temperature (approximately 0600 and 1700), as are the wind speeds.

For the period shown in Fig. 3, the valley warmed under mostly clear skies resulting in the daytime mixed layer often growing above the Peak of the mountain and incorporating the measurement site. The ability of the mixed layer height to grow above

Whistler Peak is demonstrated in the vertical profile data from 2006 discussed in section 2.2.4 and by Gallagher et al. (in press). During the nighttime, the wind speeds were usually lower than during the daytime (Fig. 3). The lower wind speeds and the relatively large forest domain mean that the Peak remained immersed in biogenic OM from the previous day. There were three periods (July 28–August 8, August 16 and August 29–31) when biomass burning contributed to the increased OM at Whistler Peak. These periods were identified by Takahama et al. (2010) using markers of

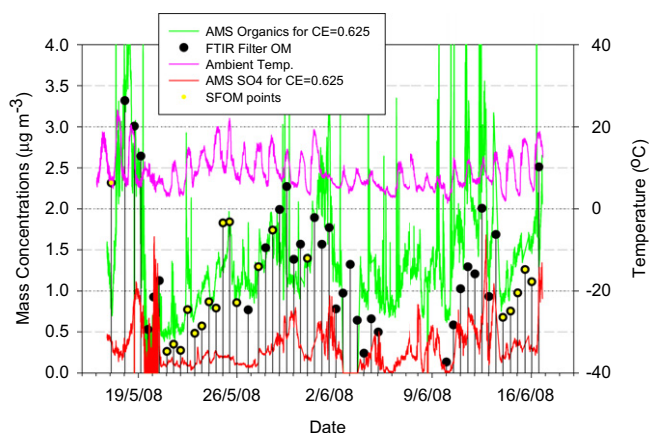


Fig. 2. Time series of ambient temperature, OM (black dots with dropped lines) and sulphate mass concentrations from the Whistler 2008 study. The sulphate mass concentrations are estimates from measurements with a High Resolution Aerosol Mass Spectrometer adjusted for the mean of the comparison with the filter OM (Schwartz et al., 2010). The black points with the yellow dots are the 20 points assigned as SFOM.

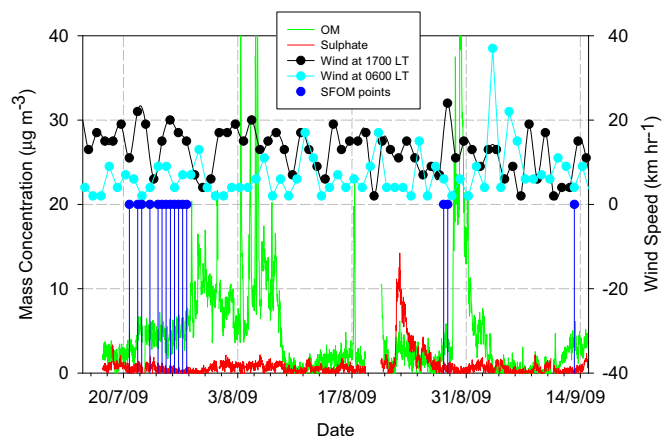


Fig. 3. Time series of organic mass (OM) concentrations, sulphate aerosol mass concentrations and wind speeds from the Whistler 2009 measurements at the peak of the mountain. The mass concentrations from the Aerosol Chemical Speciation Monitor (ACSM) are adjusted a comparison with OM from filters (Takahama et al., 2010) as discussed in text. The wind speeds are one hour averages at 0600 LT (blue dots) and at 1700 LT (black dots); the SFOA is indicated by the dark blue vertical markers (15 points).

levoglucosan in the ACSM spectra ($m/z60$ and $m/z73$; Schneider et al., 2006), changes in $m/z44:m/z43$, potassium identified on filters as well as trajectory and fire counts analyses. Takahama et al. also identify a period of non-burning biogenic influence (July 18–27) based on the absence of biomass burning indicators, the good comparison of the ACSM mass spectra with the AMS mass spectra of α -pinene ozonolysis of Shilling et al. (2009) and trajectories relative to fire counts. The first 12 SFOM points indicated in Fig. 3 are within the biogenic period identified by Takahama et al. Three additional points (August 28, night and day, and September 13) are included that fit the SFOM criteria and show no evidence of influence from biomass burning.

The 2009 SFOM concentrations given in Tables 2 and 3 are adjusted according to Equation (1). NO_x was not measured during the 2009 study. Ozone shows larger variability across the SFOM points compared with the 2007 and 2008 studies, ranging from 19 nmol mol^{-1} to 51 nmol mol^{-1} , but there is no significant difference between the mean daytime and nighttime ozone values: 33 nmol mol^{-1} and 32 nmol mol^{-1} , day and night respectively.

2.2.4. Whistler 2006

The 2006 SFOM are taken from three flights at Whistler when the valley was filled with OM and relatively little sulphate, the skies were clear and there was no significant fire influence. The profiles of OM and sulphate mass concentrations measured with the Q-AMS are shown in Fig. 4. Each 2006 SFOM point is a vertical average through 1000–2100 m. The two morning profiles are considered as nighttime points, hence the previous day maximum temperature is used, and the one afternoon profile uses the corresponding maximum temperature.

There were no significant fires in British Columbia during the weeks prior to May 14, 2006. A few fires more than 200 km to the east and north of Whistler began on May 15, but the winds at Whistler were light ($1\text{--}3 \text{ m s}^{-1}$) and southwesterly to about 2.5 km altitude and southwesterly from 2.5 km to 5.1 km. There is no evidence in the Q-AMS mass spectra of signatures of biomass burning in the form relative increases in m/z 57, 60 or 73, as discussed for the 2009 observations. Further, the mass spectra for each of these three cases all exhibit very similar m/z spectra signatures and bear relative similarities with the AMS spectra of OM from α -pinene ozonolysis for “intermediate mass loading” from Shilling et al. (2009). This analysis is consistent with that of the 2006 Whistler Peak HR-AMS data for the same period (Sun et al., 2009). The SFOM and relevant quantities are summarized in Tables 2 and 3.

2.3. Emissions models

A temperature response of the SFOM was simulated using two models based on emissions of terpenes relative to temperature. First, the terpene emissions are described by the commonly used exponential growth function (e.g. Guenther et al., 2006) for the terpene emissions activity (A_{terp}) is given by

$$A_{\text{terp}} = A_0 * e^{(\beta * (T - 303))} \quad (2)$$

where A_0 is a base emissions capacity and β is an empirical constant that is represented here by a value of 0.11 based on Goldstein et al. (2009), while noting that a value of 0.09 is also used (e.g. Schurgers et al., 2009). For comparisons with the SFOM observations, the A_{terp} are scaled using the mean SFOM value at 10°C as follows:

$$\text{SFOM}_{\text{modelled}} = \text{SFOM}_{\text{(measured at } 10^\circ\text{C)}} * A_{\text{terp}}(T)/A_{\text{terp}}(T = 10^\circ\text{C}) \quad (3)$$

Equation (3) represents the SFOM that would result as a function of temperature for a constant yield from the gas-phase oxidation of terpene and for constant meteorological conditions; i.e. assuming that the SFOM was controlled by emissions as a function of temperature only. Equation (3) describes the variation in SFOM with temperature that results from immediate conversion of emissions to OM. However, because many of the SFOM concentrations may result from the accumulation of OM over many hours to a few days, a second model is used to try to provide an upper limit to this process. The hourly temperatures over a period of 3–4 days are used to generate values of A_{terp} that are integrated to produce an accumulated OM for each hour. The integrated values are treated in the same manner as the observations in section 3: the integrated values of A_{terp} at 0600 and 1700 h were plotted with the corresponding maximum temperature and an exponential growth curve was fit to the resulting points, which was then scaled to the SFOM concentration at 10°C . The temperature data from June 9–12, 2007 at Muskoka and from June 23–27, 2009 at Whistler (933 m) were used to develop this model. Coincidentally, the three-day integration model curves that resulted from each of those temperature datasets are identical.

3. Results and discussion

3.1. SFOM changes with temperature

The SFOM concentrations versus temperature are shown in Fig. 5a, with the Egbert and Whistler points identified separately.

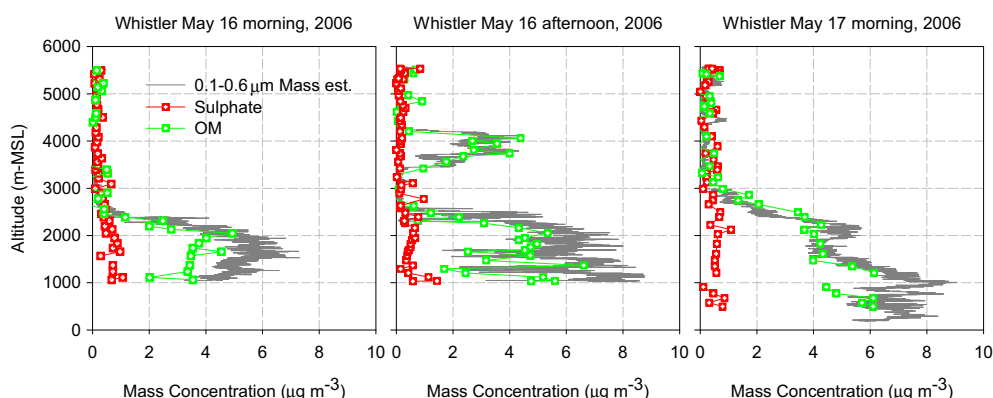


Fig. 4. Plots of the vertical profiles of OM and sulphate mass concentrations for the three cases from Whistler 2006. The grey lines are the mass concentrations estimated from integrating the size distribution measured with a PMS-PCASP optical probe assuming a total density of 1.5 g cm^{-3} (Leaitch et al., 2009). The SFOM points are calculated from the OM averaged over 1000–2100 m.

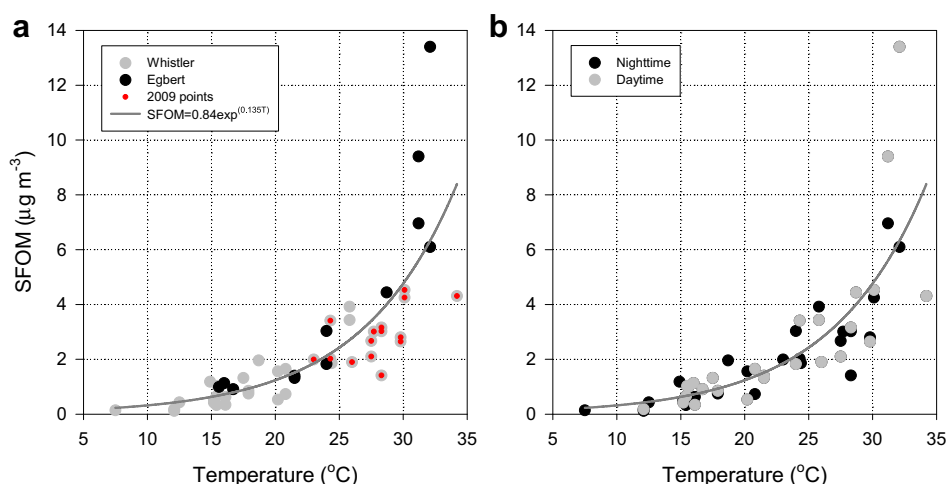


Fig. 5. The concentrations of SFOM as a function of ambient temperature: a) observations identified by site; b) observations separated between daytime (gray points) and nighttime (black points) samples. The curve in each plot is an exponential growth fit to all 50 points given in the legend of a) with an R^2 is 0.62. The red dots in a) identify the 2009 SFOM values.

An exponential growth fit, commonly used to describe BVOC emissions rates, approximates all the data points; the coefficient of determination is 0.62. The relatively greater number of points above the fit indicates that the SFOM values at Egbert were generally higher than at Whistler. Differences between the Egbert and Whistler results may reflect differences in the principal compositions of the forests impacting the two sites, differences in fetch density and in atmospheric mixing as discussed below. Separation of the SFOM data points between daytime and nighttime (Fig. 5b) shows little difference associated with time of day except for the two highest SFOM values.

At both sites, the SFOM concentrations will be reduced as the surface mixed layer deepens, commonly in the afternoon. As the mixing depth typically increases with increasing temperature, the relative estimates of SFOM at higher temperatures may be biased low. Additionally, mixing in the vertical may be inhomogeneous or incomplete, particularly toward the top of the mixed layer. This is illustrated in Fig. 4, where the aerosol concentrations are reduced at the elevation of Whistler Peak (2180 m) compared with lower in the profiles. From the 2008 study, a comparison of the number concentrations of particles in the 100–500 nm size range measured at the Peak with those measured at the 1019 m site over 18 days showed good co-variance of the concentrations ($R^2 = 0.72$), but the mean of the Peak concentrations was 56% of the values at 1019 m. Thus, it is possible that the 2009 SFOM concentrations were lower at the Peak than in the valley, which would mean they are underestimated and explain the lower 2009 SFOM values relative to the other studies; the 2009 SFOM points are identified with the red dots in Fig. 5a. The higher wind speeds at the Peak elevation during the daytime (Fig. 3) could contribute to reduced SFOM concentrations in two ways: 1) by diluting the valley aerosol as it rose above the Peak height and 2) by enhancing mixing of aerosol from the free troposphere.

Near the BVOC sources, lower wind speeds associated with high atmospheric pressure may enhance the SFOM concentrations by reduced dilution of the BVOC emissions. However, there is no evidence that the mean rise in the SFOM with increasing temperature was significantly influenced by wind speed; the slopes of linear regressions of SFOM and wind speed are near zero and the coefficients of determination are <0.02 for each of the 2007, 2008 and 2009 observations.

Variations in the data result from differences in the air fetch over the forest region (e.g. Tunved et al., 2006). The range of possibilities is addressed with the two models discussed in section

2.3. The SFOM observations versus temperature are compared with the simulated SFOM in Fig. 6a. The model based on equation (3) (blue curve) with a $\text{SFOM}_{\text{(measured at } 10^\circ\text{C)}}$ of $0.32 \mu\text{g m}^{-3}$, shows the variation with temperature expected if the SFOM concentrations were only a function of the emissions at the time of the temperature. The green curve in Fig. 6 is the result of the model that integrates the SFOM over a period of three days. The two models approximately bound the observations, which suggests that to a first approximation the SFOM precursors are represented by the terpene emissions function. Taking into consideration the possibility that many of the 2009 Whistler SFOM values are biased low, as discussed above, most of the points above 20°C show some evidence of accumulation of SFOM over some time.

The SFOM in Fig. 6a are based on a mean OM/SO₄ value of 1.52 in equation (1). The result from using 0.93 (Zhang et al., 2007), instead of 1.52, is shown in Fig. 6b. The changes are relatively small: an increase in the reference value at 10°C (0.32 to $0.43 \mu\text{g m}^{-3}$) and a slight reduction in the exponent (0.135 from 0.125).

Variations in the yield of OM from the oxidation of BVOCs will alter the pattern of SFOM with respect to temperature from the simple emissions functions. Yields of two specific BVOCs, α -pinene and limonene, are considered here because in general they comprise substantial fractions of the monoterpene emissions (e.g. Saathoff et al., 2009), insufficient information is available for other species (e.g. Hallquist et al., 2009) and they have different yields; still higher yields are associated with larger terpene molecules, such as sesquiterpenes (e.g. Lee et al., 2006; Duhl et al., 2008). The terpene emissions model (equation (3)) is scaled using OM yields from a summary of α -pinene oxidation experiments (Chan et al., 2009) as a function of temperature and the SFOM mass concentrations, where the latter are averages of the observed values and those simulated with the first model. The result is shown as the red curve in Fig. 6b. The curve that results from applying the higher yields from the oxidation of limonene (Saathoff et al., 2009) is the yellow curve in Fig. 6b. These curves move in the direction from the simple constant-yield terpene emissions model (blue curve) toward the fit to the observations and this is another factor that may enhance the SFOM concentrations at higher temperatures.

Additional factors, not already discussed, that may have affected the SFOM concentrations relative to temperature are as follows:

- Changes in oxidant levels with temperature – Ozone, the only oxidant measured here, is only weakly associated with

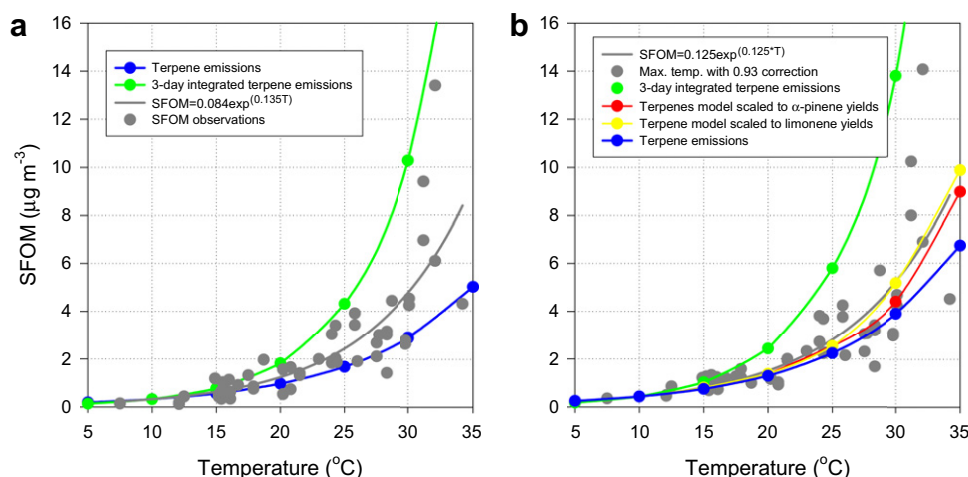


Fig. 6. a) SFOM observations and modeled SFOM. The modeled SFOM is based on the straight terpenes emissions function based on equation (2) (blue curve) and on the integrated terpenes emissions model described in the text (green curve). The modeled curves are scaled to the observations mean SFOM of $0.32 \mu\text{g m}^{-3}$ at 10°C . b) as a), but for the observations using a value of OM/SO₄ of 0.93 (from Zhang et al., 2007) in equation (1) (see section 2.2), and the modeled curves are scaled to the mean of the SFOM observations at 10°C ($0.43 \mu\text{g m}^{-3}$). Terpene emissions-only (blue), terpene emissions scaled to yields for α -pinene oxidized by ozone (red) and for limonene oxidized by ozone (yellow). The percentage yields used to scale the terpene emissions model are: 7.5% at 5°C and $0.18 \mu\text{g m}^{-3}$, 7.5% at 10°C and $0.32 \mu\text{g m}^{-3}$, 7.5% at 15°C and $0.6 \mu\text{g m}^{-3}$, 8% at 20°C and $1.2 \mu\text{g m}^{-3}$, 8.5% at 25°C and $2.1 \mu\text{g m}^{-3}$, 8.5% at 30°C and $3.8 \mu\text{g m}^{-3}$ and 10% at 35°C and $7.0 \mu\text{g m}^{-3}$ for oxidation of α -pinene (Chan et al., 2009); 15% at 5°C and $0.18 \mu\text{g m}^{-3}$, 15% at 10°C and $0.32 \mu\text{g m}^{-3}$, 16% at 15°C and $0.6 \mu\text{g m}^{-3}$, 16% at 20°C and $1.2 \mu\text{g m}^{-3}$, 17% at 25°C and $2.1 \mu\text{g m}^{-3}$, 20% at 30°C and $3.8 \mu\text{g m}^{-3}$ and 22% at 35°C and $7.0 \mu\text{g m}^{-3}$ for oxidation of limonene (Saathoff et al., 2009).

increasing temperature (R^2 of 0.03 and 0.19 for daytime and nighttime points respectively) and its pattern of increase is unlike that of the SFOM. The OH radical has been suggested to be the limiting factor for some biogenic products (Zhang et al., 2010), but this can not be evaluated using the present observations.

- Relative humidity – The RH can be a significant factor for biogenic aerosol production at atmospheric temperatures much lower than the present observations (Jonsson et al., 2008; Saathoff et al., 2009; Tillmann et al., 2010), but for the present temperatures there is no evidence for a significant influence from RH on biogenic aerosol production (e.g. Cocker et al., 2001). A simple regression of the SFOM with RH also shows no evidence of a significant association; however, the limited size of the dataset and the dominant association with temperature make it impossible to preclude effects from RH.
- Dust – The SFOM will be underestimated due to attachment to suspended dust as well as dry deposition to the ground and foliage. Dust is more prevalent during warmer conditions at Whistler, and there is evidence for OM on suspended coarse

particles at Whistler (Schwartz et al., 2010); although it is unclear how much of it is of secondary biogenic origin.

- Isoprene – A regional model was able to account for most of the 2007 SFOM by terpene emissions with approximately a 7% contribution from isoprene (Slowik et al., 2010). For Whistler, the relative contribution from isoprene is estimated by considering a combination of the measured mixing ratios of isoprene and terpenes and their relative oxidation rates. Isoprene and monoterpenes were measured during the Whistler 2008 study (Schwartz et al., 2010) and during the summer of 2001 in Golden Ears Provincial Park about 100 km south of Whistler (Shantz et al., 2004). The maximum ratio of the mean values of isoprene and monoterpenes from those studies (Table 4) is 0.27, and the range of the oxidation rates of isoprene relative to the selected terpenes 0.05–2 (Table 4). Combined, these two factors give an upper estimate for the emissions of isoprene relative to monoterpenes of 0.5. Taking into account the relative yields of OM from isoprene oxidation (1%–4%: Carlton et al., 2009) compared terpene oxidation (8%–30%: Saathoff et al., 2009; Chan et al., 2009), the maximum contribution to the SFOM from isoprene is estimated at 6% of the terpene contribution. Despite the small fraction here, isoprene emissions increase with temperature faster than terpene emissions, and the relative contribution from isoprene may increase with temperature.

Table 4

Terpene and isoprene mean values and rate constants for selected BVOCs reacting with O₃, OH or NO₃.

| Observations | | | |
|---------------------------------------|---|---|--|
| | Terpene mixing ratio (pptv) | Isoprene mixing ratio (pptv) | |
| Golden Ears; Shantz et al. (2004) | 810 | 100 | |
| Whistler 2008; Schwartz et al. (2010) | 130 (220) | 35 (49) | |
| Selected BVOC rate constants | | | |
| Oxidant | O ₃ (cm ³ molecule ⁻¹ s ⁻¹) | OH (cm ³ molecule ⁻¹ s ⁻¹) | NO ₃ (cm ³ molecule ⁻¹ s ⁻¹) |
| Reactant | | | |
| a-Pinene | 86.6×10^{-18} | 53.7×10^{-12} | 0.62×10^{-11} |
| b-Pinene | 15×10^{-18} | 78.9×10^{-12} | 0.25×10^{-11} |
| Limonene | 200×10^{-18} | 164×10^{-12} | 1.22×10^{-11} |
| Isoprene | 12.8×10^{-18} | 101×10^{-12} | 0.07×10^{-11} |

Values are project means. Values in parentheses are means for periods identified as biogenic episodes.

Values at 298 K from Seinfeld and Pandis (2006); taken from Atkinson (1994).

4. Conclusions

Observations at two temperate forest sites in both western and eastern Canada offer the first estimation of how the concentrations of submicron forest organic aerosol mass (SFOM) from the oxidation of biogenic volatile organic compounds (BVOC) vary over the ambient temperature range of 7°C to 34°C . The range of the SFOM concentrations increases with increasing temperature, constrained on the lower end by the standard terpene emissions function and on the upper end by a model of the accumulation of SFOM over a few days that is also based on the standard terpene emissions function. The results are summarized as follows:

1. The model that is commonly used to define terpene emissions is able to constrain these SFOM observations assuming a constant yield of OM from BVOC oxidation.
2. The agreement of the observations and model is improved through the application of an increased yield of SFOM as the organic mass concentration increases with temperature that is based on results from chamber studies. Thus, the SFOM yield may be enhanced at higher temperatures.
3. The large range of SFOM concentrations at higher temperatures leaves open a number of questions, including the relative contributions of changing yield and of isoprene, that may be addressed by more ambient observations at higher temperatures.

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References

- Andreae, M.O., Crutzen, P.J., 1997. Atmospheric aerosols: biogeochemical sources and role in atmospheric chemistry. *Science* 276, 1052–1058.
- Atkinson, R., 1994. Gas-phase tropospheric chemistry of organic compounds. *J. Phys. Chem. Ref. Data*, 1–216. Monograph No. 2.
- Carlton, A.G., Wiedinmyer, C., Kroll, J.H., 2009. A review of Secondary Organic Aerosol (SOM) formation from isoprene. *Atmos. Chem. Phys.* 9, 4987–5005.
- Carlsaw, K.S., Boucher, O., Spracklen, D.V., Mann, G.W., Rae, J.G.L., Woodward, S., Kulmala, M., 2010. A review of natural aerosol interactions and feedbacks within the Earth system. *Atmos. Chem. Phys.* 10, 1701–1737.
- Chan, M.N., Chan, A.W.H., Chhabra, P.S., Surratt, J.D., Seinfeld, J.H., 2009. Modeling of secondary organic aerosol yields from laboratory chamber data. *Atmos. Chem. Phys.* 9, 5669–5680.
- Chan, T.W., Huang, L., Leitch, W.R., Sharma, S., Brook, J.R., Slowik, J.G., Abbatt, J.P.D., Brickell, P.C., Liggio, J., Li, S.M., Moosmüller, H., 2010. Determination of OM/OC ratios and specific attenuation coefficients (SAC) in ambient fine PM at a rural site in southern Ontario: implications for emission sources, particle aging, and radiative forcing. *Atmos. Chem. Phys.* 10, 1–19.
- Claeys, M., et al., 2004. Formation of secondary organic aerosols through photo-oxidation of isoprene. *Science* 303, 1173–1176.
- Cocker, David R., III, Clegg, Simon L., Flagan, Richard C., Seinfeld, John H., 2001. The effect of water on gas–particle partitioning of secondary organic aerosol. Part I: α -pinene/ozone system. *Atmos. Environ.* 35, 6049–6072.
- Drewnick, F., et al., 2005. A new time-of-flight aerosol mass spectrometer (ToF-AMS)—instrument description and first field deployment. *Aerosol Sci. Technol.* 39, 637–658. doi:10.1080/02786820500182040.
- Duhl, T.R., Helmig, D., Guenther, A., 2008. Sesquiterpene emissions from vegetation: a review. *Biogeosciences* 5, 761–777.
- Fowler, D., et al., 2009. Atmospheric composition change: ecosystems–atmosphere interactions (Review). *Atmos. Environ.* 43, 5193–5267.
- Gallagher, J.P., McKendry, I.G., Macdonald, A.M., Leitch, W.R. Seasonal and diurnal variations in aerosol concentration on Whistler Mountain: boundary layer influence and synoptic scale controls. *J. Appl. Meteorol. Climatol.*, in press.
- Guenther, A., et al., 2006. Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature). *Atmos. Chem. Phys.* 6, 3181–3210.
- Goldstein, A.H., Galbally, I.E., 2007. Known and unexplored organic constituents in the earth's atmosphere. *Environ. Sci. Technol.* 41, 1514–1521.
- Goldstein, A.H., Koven, C.D., Heald, C.L., Fung, I.Y., 2009. Biogenic carbon and anthropogenic pollutants combine to form a cooling haze over the southeastern United States. *Proc. Natl. Acad. Sci. U.S.A.* 106, 8835–8840.
- Hallquist, M., et al., 2009. The formation, properties and impact of secondary organic aerosol: current and emerging issues. *Atmos. Chem. Phys.* 9, 5155–5236.
- Heald, C.L., et al., 2008. Predicted change in global secondary organic aerosol concentrations in response to future climate, emissions, and land use change. *J. Geophys. Res.* 113, D02307.
- Jayne, J.T., et al., 2000. Development of an aerosol mass spectrometer for size and composition analysis of submicron particles. *Aerosol Sci. Technol.* 33, 49–70.
- Jonsson, A.M., Hallquist, M., Ljungström, E., 2008. The effect of temperature and water on secondary organic aerosol formation from ozonolysis of limonene, Δ^3 -carene and α -pinene. *Atmos. Chem. Phys.* 8, 6541–6549.
- Kiendler-Scharr, A., et al., 2009. New particle formation in forests inhibited by isoprene emissions. *Nature* 461, 381–384.
- Kroll, J.H., Ng, N.L., Murphy, S.M., Flagan, R.C., Seinfeld, J.H., 2005. Secondary organic aerosol formation from isoprene photooxidation under high-NO_x conditions. *Geophys. Res. Lett.* 32, L18808.
- Lindinger, W., Hansel, A., Jordan, A., 1998. Proton-transfer reaction mass spectrometry (PTR-MS): on-line monitoring of volatile organic compounds at pptv levels. *Chem. Soc. Rev.* 27, 347–354.
- Liu, P.S.K., Deng, R., Smith, K.A., Williams, L.R., Jayne, J.T., Canagaratna, M.R., Moore, K., Onasch, T.B., Worsnop, D.R., Deshler, T., 2007. Transmission efficiency of an aerodynamic focusing lens system: comparison of model calculations and laboratory measurements for the Aerodyne Aerosol Mass Spectrometer. *Aerosol Sci. Technol.* 41, 721–733.
- Leitch, W.R., et al., 2009. Evidence for Asian dust effects from aerosol plume measurements during INTEX-B 2006 near Whistler, BC. *Atmos. Chem. Phys.* 9, 3523–3546.
- Lee, A., Goldstein, A.H., Kroll, J.H., Ng, N.L., Varutbangkul, V., Flagan, R.C., Seinfeld, J.H., 2006. Gas-phase products and secondary aerosol yields from the photooxidation of 16 different terpenes. *J. Geophys. Res.* 111, D17305. doi:10.1029/2006JD007050.
- Liggio, J., Li, S.M., Vlasenko, A., Sjøstedt, S., Chang, R., Shantz, N., Abbatt, J., Slowik, J.G., Bottenheim, J.W., Brickell, P.C., Stroud, C., Leitch, W.R., 2010. Primary and secondary organic aerosols in urban air masses intercepted at a rural site. *J. Geophys. Res.* 115, doi:10.1029/2010JD014426.
- Matthew, B.M., Middlebrook, A.M., Onasch, T.B., 2008. Collection efficiencies in an aerodyne aerosol mass spectrometer as a function of particle phase for laboratory generated aerosols. *Aerosol Sci. Technol.* 42, 884–898.
- Ng, N.L., Herndon, S.C., Trimborn, A., Canagaratna, M.R., Croteau, P., Onasch, T.B., Sueper, D., Worsnop, D.R., Zhang, Q., Sun, Y.L., Jayne, J.T., 2011. An Aerosol Chemical Speciation Monitor (ACSM) for routine monitoring of the composition and mass concentrations of ambient aerosol. *Aerosol Sci. Technol.* 45, 780–794.
- Pankow, J.F., 1994. An absorption model of the gas/aerosol partitioning involved in the formation of secondary organic aerosol. *Atmos. Environ.* 28, 189–193.
- Russell, L.M., 2003. Aerosol organic-mass-to-organic-carbon ratio measurements. *Environ. Sci. Technol.* 37, 2982–2987.
- Saathoff, H., et al., 2009. Temperature dependence of yields of secondary organic aerosols from the ozonolysis of α -pinene and limonene. *Atmos. Chem. Phys.* 9, 1551–1577.
- Schneider, J., et al., 2006. Mass spectrometric analysis and aerodynamic properties of various types of combustion-related aerosol particles. *Int. J. Mass Spectrom.* 258, 37–49.
- Schurgers, G., Arnecht, A., Holzinger, R., Goldstein, A.H., 2009. Process-based modelling of biogenic monoterpene emissions combining production and release from storage. *Atmos. Chem. Phys.* 9, 3409–3423.
- Schwartz, R.E., et al., 2010. Biogenic oxidized organic functional groups in aerosol particles from a mountain forest site and their similarities to laboratory chamber products. *Atmos. Chem. Phys.* 10, 5075–5088.
- Seinfeld, J.H., Pandis, S.N., 2006. *Atmospheric Chemistry and Physics*, second ed. Wiley-Interscience, New York, NY, USA, pp. 43–46.
- Shantz, N.C., Aklilu, Y.A., Ivanis, N., Leitch, W.R., Brickell, P.C., Brook, J.R., Cheng, Y., Halpin, D., Li, S.M., Tham, Y.A., Toom-Saunty, D., Prenni, A.J., Graham, L., 2004. Chemical and physical observations of particulate matter at Golden Ears Provincial Park from anthropogenic and biogenic sources. *Atmos. Environ.* 38, 5849–5860.
- Shilling, J.E., Chen, Q., King, S.M., Rosenoern, T., Kroll, J.H., Worsnop, D.R., DeCarlo, P.F., Aiken, A.C., Sueper, D., Jimenez, J.L., Martin, S.T., 2009. Loading-dependent elemental composition of α -pinene SOM particles. *Atmos. Chem. Phys.* 9, 771–782.
- Slowik, J.G., et al., 2010. Characterization of a large biogenic secondary organic aerosol event from eastern Canadian forests. *Atmos. Chem. Phys.* 10, 2825–2845.
- Spracklen, D.V., Bonn, B., Carlsaw, K.S., 2008. Boreal forests, aerosols and the impacts on clouds and climate. *Phil. Trans. R. Soc. A.* doi:10.1098/rsta.2008.0201.
- Sun, Y., Zhang, Q., MacDonald, A.M., Hayden, K., Li, S.M., Liggio, J., Liu, P.S.K., Anlauf, K.G., Leitch, W.R., Cubison, M., Worsnop, D., van Donkelaar, A., Martin, R.V., 2009. Size-resolved aerosol chemistry on Whistler Mountain, Canada with a High-Resolution Aerosol Mass Spectrometer during INTEX-B. *Atmos. Chem. Phys.* 9, 3095–3111. www.atmos-chem-phys.net/9/3095/2009.
- Takahama, S., Schwartz, R.E., Russell, L.M., Macdonald, A.M., Sharma, S., Leitch, W.R., 2010. Organic Functional Groups in Aerosol Particles from Burning and Non-burning Forest Emissions at a High-Elevation Mountain Site. *ACPD*.
- Tillmann, R., Hallquist, M., Jonsson, A.M., Kiendler-Scharr, A., Saathoff, H., Iinuma, Y., Mentel, Th. F., 2010. Influence of relative humidity and temperature on the production of pinonaldehyde and OH radicals from the ozonolysis of α -pinene. *Atmos. Chem. Phys.* 10, 7057–7072. www.atmos-chem-phys.net/10/7057/2010/ doi:10.5194/acp-10-7057-2010.
- Tsigaridis, K., Kanakidou, M., 2007. Secondary organic aerosol importance in the future atmosphere. *Atmos. Environ.* 41, 4682–4692.
- Tunved, P., et al., 2006. High natural aerosol loading over boreal forests. *Science* 312, 261–263.
- Vlasenko, A., et al., 2009. Measurements of VOCs by proton transfer reaction mass spectrometry at a rural Ontario site: sources and correlation to aerosol composition. *J. Geophys. Res. Atmos.* 114, D21305. doi:10.1029/2009JD012025.
- Went, F.W., 1960. Blue hazes in the atmosphere. *Nature* 187, 641–643.
- Zhang, Q., et al., 2007. Ubiquity and dominance of oxygenated species in organic aerosols in anthropogenically-influenced Northern Hemisphere midlatitudes. *Geophys. Res. Lett.* 34, L13801.
- Zhang, Y.Y., Muller, L., Winterhalter, R., Moortgat, G.K., Hoffmann, T., Poschl, U., 2010. Seasonal cycle and temperature dependence of pinene oxidation products, dicarboxylic acids and nitrophenols in fine and coarse air particulate matter. *Atmos. Chem. Phys.* 10, 7859–7873.