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Monoterpene emissions from a Pacific Northwest Old-Growth Forest and impact on regional biogenic VOC emission estimates

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Abstract

Measurements of natural hydrocarbon emission rates are reported for an old-growth Pacific Northwest coniferous forest. The emission data were collected for the two dominant species Douglas-fir (*Pseudotsuga menziesii*) and western hemlock (*Tsuga heterophylla*) during the growing season in 1997 and 1998 using branch enclosure techniques. Samples were collected at different heights from 13 to 51 m within the canopy using the Wind River Canopy Crane facility. The standard emission factor at a temperature of 30°C and the temperature coefficient for Douglas-fir is $E_s = 0.39 \pm 0.14\,\mu g\,C\,g^{-1}\,h^{-1}$ and $\beta = 0.14 \pm 0.05°C^{-1}$ and for western hemlock $E_s = 0.95 \pm 0.17\,\mu g\,C\,g^{-1}\,h^{-1}$ and $\beta = 0.06 \pm 0.02°C^{-1}$. There was considerable variability among all the emission factors due to seasonal and branch-to-branch variations. Within season emission factors appear to decline from May to September for the Douglas-fir, although there was no corresponding decrease for the western hemlock. There was no significant difference in standard emission factors (E_s) or temperature coefficients as a function of sunlit versus shady growth environment (different heights) for Douglas-fir, but western hemlock emission samples collected low in the canopy showed no exponential correlation with temperature. Applying the standard emission factors from this study to a Pacific Northwest domain and comparing the modified emission inventory to the current regulatory-based emission inventory yielded a net decrease of 19% in the domain wide monoterpene emissions. The relatively small difference in biogenic emissions is slightly misleading, as the difference in standard emission rates between this study and current regulatory rates is quite significant, and they offset each other when combined in this domain. When this inventory was input into a regional photochemical air quality simulation using the MM5/CMAQ system, the reduction in biogenic emissions resulted in an insignificant decrease of O_3 and a significant decrease in the secondary organic aerosol (domain wide −20%). The emission measurements reported here represent one of the first extensive data sets for an old-growth forest, where sampling conditions are limited to in situ enclosure techniques within the tall, elevated canopy.

Keywords: Douglas-fir; Western hemlock; Enclosure method; Secondary biogenic aerosol; Ozone

1. Introduction

Monoterpenes are estimated to account for 11% of the annual global biogenic volatile organic compound (BVOC) flux (Guenther et al., 1995) and 25% of the total North American non-methane VOC flux

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(Guenther et al., 2000). Monoterpenes are oxidized in photochemical processes that lead to the formation of tropospheric ozone and secondary organic aerosols (SOA) that contribute to regional haze, reduced visibility, and changes to the global radiation budget (Fehsenfeld et al., 1992; Griffin et al., 1999; Calogirou et al., 1999; Atkinson, 2000).

Biogenic emission inventories are developed using canopy models with input parameters such as above canopy temperature, radiation, wind speed, and relative humidity, along with an empirical relationship based on the species-specific standard emission rate and environmental conditions (Guenther et al., 2000; Lindfors et al., 2000). The canopy model coupled with land-use characteristics, species composition and biomass density provides hourly, gridded estimates of BVOC emissions. Photochemical model results for ozone as well as SOAs are sensitive to BVOC emissions (Pun et al., 2002; Hanna et al., 2001; Pierce et al., 1998). Typical photochemical models treat all monoterpene emissions the same, assuming their fate in the atmosphere is similar. However, studies have shown that individual monoterpene compounds react differently and have aerosol yields that vary significantly from each other (Hoffmann et al., 1997; Atkinson, 2000; Hallquist et al., 1999). Gaining a better understanding of BVOC emissions is, thus, important for determining the appropriate regulatory oxidant control strategies (e.g., NO_x vs. VOC reductions) (Trainer et al., 2000), and for correctly modeling atmospheric aerosol formation from the oxidation of monoterpene emissions (Hallquist et al., 1999; Geron et al., 2000). Lastly, researchers are currently developing real-time air quality forecasting systems in which BVOC emission inventories will be important (Vaughan et al., 2004).

Uncertainty associated with developing biogenic hydrocarbon (BHC) emission inventories stems from several factors including the species-specific standard emission rates (Geron et al., 2000). Additional uncertainties may be introduced when standard emission rates measured from young trees (typically <3 years old) in a greenhouse environment are applied to canopies that can range in age up to 500 years (Street et al., 1997; Adams and Hagerman, 1976) and have varying environments from year-to-year. Recently attention has been directed towards understanding the changes to the structure and function of a forest canopy as it ages (Bond and Franklin, 2002). For example, if there are age-related changes in leaf structure, CO_2 assimilation rates, nitrogen concentration, canopy structure and stand productivity, will biogenic emissions differ from those measured at younger stands? Progress has been made in developing reliable micrometeorological techniques for measuring canopy scale monoterpene fluxes (Rinne et al., 2002; Schween et al., 1997); however, determining species-specific standard emission rates requires enclosure techniques. In addition, understanding physiological controls of monoterpene emissions (such as differences in emission rates from various heights within the canopy) requires detailed spatial sampling techniques not available with above canopy flux measurements.

This paper presents first results of in situ monoterpene emission measurements from various heights within the canopy of an old-growth forest. Measurements were made throughout the summer growing season over a span of 2 years with enclosure techniques. Our specific objectives were: (1) to obtain emission rate measurements of monoterpenes from the principal coniferous species at the site (Douglas-fir and western hemlock), (2) to examine the emission patterns as a function of environmental conditions, position in the canopy, and time of year, and (3) to estimate the impact of measured emissions from a mature forest on regional estimates of BVOC emissions and the corresponding impact on regional air quality. Objectives 1 and 2 meet specific goals outlined in work presented by Geron et al. (2000) where US tree species are ranked by their monoterpene relative emission potential (REP), or importance as a monoterpene emitter. Douglas-fir is listed within the top 10 tree species that are very important monoterpene emitters nationally. To address objective 3, we modified a regional biogenic emission inventory using our measured emissions and used the revised inventory in a simulation of photochemical air quality for the Pacific Northwest.

2. Experimental methods

Measurements were conducted at the Wind River Canopy Crane Research Facility (WRCCRF) in Carson, Washington (Lat. 45° 49′ N, Long. 121° 57′ W). The WRCCRF is located within an undisturbed 478-ha old-growth temperate rainforest with trees estimated to be 500 years old (Shaw et al., 2004). Within the center of the WRCCRF is a 75-m freestanding construction tower crane. The crane provides three-dimensional access to the canopy within a 2.3-ha area that enables the collection of samples at various heights within the canopy. This research area exemplifies a typical Pacific Northwest ecosystem, composed predominantly of Douglas-fir (*Pseudotsuga menziesii*) and western hemlock (*Tsuga heterophylla*). Biomass estimates for the 4-ha crane plot indicate that western hemlock comprises 32%, and Douglas-fir 50% of the biomass (Harmon et al., 2004).

We conducted field campaigns approximately every 3.5 weeks during the summer growing seasons of 1997 and 1998 (June through September). Monoterpene emissions were measured from 4 branches on one Douglas-fir tree and from 4 branches on one western

hemlock tree using an enclosure technique. The branches selected for sampling were on the north side of each tree, with one each at the top, middle, and bottom of the crown, plus one sample location on the south side of each tree. All eight branches were flagged and the same branches were sampled throughout the entire summer. The same two trees were sampled the second summer; however, eight different branches were selected. Approximately nine samples from each tree during each campaign were collected to quantify monoterpene emission rates. Thus, a total of 106 samples were collected from 8 Douglas-fir branches (one tree), and 89 emission samples were collected from 8 western hemlock branches (one tree) over both seasons.

Three different types of enclosures were used throughout this study, and a comparison was done between results for two of the enclosures. A Teflon bag, the Li-Cor 6200 4-L chamber and the Li-Cor 6400 conifer chamber were used during the study, and the comparison was done during the summer of 1998 between the Li-Cor 6400 chamber and a Teflon bag enclosure. The bag enclosure technique was used to minimize artifact peaks caused by off-gassing from the Li-Cor chamber materials, and to provide a second type of enclosure that may possibly reduce the amount of needle damage caused by chamber enclosure techniques (Juuti et al., 1990). Extreme care was taken when placing the chamber (or bag) around the branch not to disturb the needles. The chamber (or bag) was placed on the branch at the same location each time, and the chamber (or bag) was sealed around the bare stem without crushing any needles. All of the enclosures were continuous open-flow systems with a flush gas comprised of ambient air scrubbed of hydrocarbons using a charcoal trap (Alltech). The systems were adapted with an external diaphragm pump (KNF Neuberger) to pump a fraction of the exhaust gas from the chamber to flush and fill one-L dual-valve electro polished stainless steel canisters for VOC (monoterpene) analysis. Flow rates entering the enclosures were greater than the VOC sample flow rates creating a slight positive pressure inside the enclosure and eliminating leaks into the chamber. Both enclosure systems (the 6200 and the 6400) were tested in the laboratory with pressure gauges and smoke tests to confirm that chamber pressures and internal mixing within each chamber were adequate. Quantum sensors (LI-190SA, Li-Cor) were mounted on the side of each chamber for photosynthetic photon flux density (PPFD) measurements. Samples in 1998 were collected from branches side-by-side using the Li-Cor 6400 and a Teflon bag. No obvious bias was found between these two sampling techniques; roughly half of the bag samples (38 out of 72) had VOC concentrations higher than the paired chamber samples and roughly half (34 out of 72) were less than the paired chamber samples. Branch to branch variability precluded the use of a statistically formal paired analysis. More details are presented in Pressley (1999).

At the end of each summer, the sampled branches were clipped, frozen, and returned to Washington State University for analysis. One sided needle area was calculated for each class of needle (current terminal growth versus older needles) using a Li-Cor 3100 leaf area meter. Errors associated with instrument precision were $<1\%$ for all samples. After leaf area was determined, needles were oven dried at $60^{\circ}C$ for 48 h and weighed VOC. All sampling was done after needle elongation was complete, and it was assumed that biomass did not change significantly throughout the sampling period.

Samples from the stainless steel canisters were analyzed on-site using gas chromatography (HP5890 GC or HP5880 GC) with DB-1 (30-m long $\times$ 32-mm I.D.) capillary column (J & W), and flame ionization detection (FID). The sample-to-analysis time was <8 h to reduce isomerization within the sample canister from one monoterpene compound to another. All samples were cryogenically pre-concentrated before injection (or GC analysis). Monoterpenes identified during the summer of 1997 included α-pinene, β-pinene, Δ^3-carene (hereafter, Δ-carene), and limonene. The list of identifiable compounds was enlarged during the summer of 1998 to include camphene, and myrcene. A standard containing isoprene and various monoterpenes (Scott-Marrin) was analyzed each sampling day for quantifying retention times and standard concentrations were referenced with a standard of 2, 2-dimethylbutane (C_6H_{19}). Humidity levels of the samples in the canisters (due to transpiration of the needles) averaged 55%, with the lowest being 29% during the middle of the summer in 1998. Throughout the field campaigns, random cans were selected for duplicate analysis to confirm sample integrity, and samples were collected from an empty enclosure (no biomass) to ensure there was no contamination between samples. Errors associated with GC precision were $<\pm 8\%$. Emission rates (in $\mu g\,C\,g^{-1}\,h^{-1}$) are reported at ambient conditions based on the dry weight of the enclosed foliar biomass, so that emission rates were $E_{meas} = CQ/B$ where C is the monoterpene concentration in carbon (C) equivalents ($\mu g\,C\,m^{-3}$) in the chamber air, Q is the flush air flow rate ($m^3\,h^{-1}$), and B is the dry needle biomass (g) obtained at the end of the sampling period.

3. Results and discussion

3.1. Emissions

Of the total identified monoterpene emissions, α-pinene comprised 51% of the total for Douglas-fir and

38% of the total emissions for western hemlock. The second most abundant monoterpene was β-pinene, which averaged 26% of the total for Douglas-fir and 22% of the total emissions for western hemlock. In all samples, α-pinene, β-pinene, and limonene together comprised more that 64% of the total identified monoterpene emissions. Similar findings were reported by Lerdau et al. (1995) for 3-year Douglas-fir seedlings with the exception that α-pinene, β-pinene, and Δ-carene (not limonene) composed more than 95% of the emissions. In contrast, historical studies showed that in some of the western conifer species (Douglas-fir included) β-pinene and/or Δ-carene are the dominant terpenes emitted (Geron et al., 2000; Lerdau et al., 1995, 1994; Janson, 1993; Komenda and Koppmann, 2002). No reports have been published for monoterpene emission compositions from western hemlock.

The total monoterpene emission rates for Douglas-fir varied from about $0.01\,\mu g\,C\,g^{-1}\,h^{-1}$ at temperatures around 14°C to a maximum of $4.5\,\mu g\,C\,g^{-1}\,h^{-1}$ measured at 40°C. The total monoterpene emission rates for western hemlock varied from $0.07\,\mu g\,C\,g^{-1}\,h^{-1}$ at temperatures near 15°C to $6.26\,\mu g\,C\,g^{-1}\,h^{-1}$ measured at 42°C. In addition to varying sampling conditions, there were also branch-to-branch variations (4 locations within the crown of the canopy) in the measured emissions similar to past studies (Lerdau et al., 1994; Komenda and Koppmann, 2002). The emission characteristics of each individual monoterpene varied with conditions. Table 1 presents the correlation coefficients (R^2) determined for the measured emission rates of individual monoterpenes versus the measured emission rate of α-pinene. There is large variability in the correlations, which can be expected if one considers that the samples were collected from different branches with different growth environments (e.g. sun vs. shade). However, there are some surprisingly strong emission rate correlations, such as the β-pinene and limonene correlations with α-pinene for the western hemlock samples.

Monoterpene emissions from most plants are known to increase exponentially with temperature (Tingey et al., 1980; Juuti et al., 1990; Guenther et al., 1993). Standard emission factors (sometimes referred to as basal emission rates) are typically calculated using the Guenther et al. (1993) algorithm; $E_{meas} = E_s \exp[\beta(T - T_s)]$ that normalizes the measured emission rates at ambient temperatures to a standard temperature of 30°C. In this equation, E_{meas} is the measured emission rate at leaf temperature T (°C), E_s is the emission rate at standard temperature T_s (30°C) and β ($^\circ C^{-1}$) is an empirical temperature coefficient ranging from $0.06^\circ C^{-1}$ to $0.14^\circ C^{-1}$, with an average value of $0.09^\circ C^{-1}$. Standard emission factors (E_s) and the empirical coefficients (β) for the individual compounds normalized to 30°C were all determined using this equation.

Emission rates generally fit the emission algorithm well when a small subset of samples is selected. For example, monoterpenes sampled from the uppermost Douglas-fir branches 27 and 28 July 1998 exhibited an exponential increase of emissions with temperature. Table 2 summarizes the results for β and E_s for each of the monoterpenes. All of the monoterpenes except for β-pinene ($R^2 = 0.28$) showed a significant linear correlation between the logarithmic emission rate and the temperature deviation from the standard temperature. Temperature dependence parameters were not statistically different between each of the monoterpenes based on a 95% confidence interval. Monoterpene emissions did not show a correlation with historical temperature means (i.e. 1, 2, 3, 5, and 7 day running mean) or with PPFD values.

Table 1
Correlation coefficients (R^2) for the emission rates of specific monoterpenes vs. the emission rate of α-pinene for each sampling year and combined sampling years differentiated by species

	Douglas-fir (1997)	*n*	Douglas-fir (1998)	*n*	Douglas-fir (1997–1998)	*n*
β-Pinene	0.452	27	0.597	78	0.411	105
Δ-Carene	0.03	15	0.694	53	0.042	68
Limonene	0.353	15	0.746	78	0.602	93
Myrcene			0.577	62		
Camphene			0.561	34		
	Hemlock (1997)	*n*	Hemlock (1998)	*n*	Hemlock (1997–1998)	*n*
β-Pinene	0.919	31	0.329	58	0.368	89
Δ-Carene			0.105	13		
Limonene	0.919	30	0.229	58	0.209	88
Myrcene			0.264	57		
Camphene			0.709	25		

Results include samples from all locations and all enclosure types, and *n* is the number of enclosure samples.

Table 2
Standard emission factors and temperature-dependence parameters plus the 95% confidence interval determined using $[\ln E_{meas} = \ln E_s + \beta(T - T_s)]$, where β ($^\circ C^{-1}$) is the slope of the line and E_s ($\mu g\, C\, g^{-1}\, h^{-1}$) is calculated from the y-intercept

	Standard emission factor (E_s)	Temperature-dependence parameter (β)	Correlation coefficient (R^2) and number of samples (n)
α-Pinene	0.144 (0.07–0.32)	0.286±0.136	0.75 (9)
β-Pinene	0.076 (0.03–0.17)	0.108±0.142	0.28 (9)
Limonene	0.022 (0.01–0.04)	0.166±0.089	0.70 (9)
Δ-Carene	0.013 (0.01–0.02)	0.112±0.064	0.71 (8)
Myrcene	0.021 (0.01–0.04)	0.297±0.117	0.84 (8)
Camphene	0.006 (0.0–0.01)	0.168±0.097	0.85 (6)
Sum terpenes	0.312 (0.14–0.69)	0.226±0.136	0.65 (9)

Results are from nine enclosure samples collected over 2 days (27 and 29 July 1998) from the top branches of a Douglas-fir tree. Two different branches were sampled (one with the LiCor 6400 enclosure and one with the bag enclosure.

3.2. Seasonal emission patterns

Temperature-independent seasonal variability of monoterpene emissions have been explored in several different ecosystems (Janson, 1993; Lerdau et al., 1997). Both the composition of emissions and the amount of total monoterpene emissions changes throughout the season depending on needle age (Flyckt, 1979; Lerdau et al., 1995). During the course of the two summers, there appears to be a general decline in standard emission factors for Douglas-fir, but no seasonal change for hemlock. There were three field campaigns in 1997 (July–September) and four field campaigns in 1998 (June–September). In order to remove some of the scatter caused by branch-to-branch variation, samples were sorted by branch (location) and grouped by field campaign, and the natural logarithm of the sum of monoterpenes was plotted vs. the temperature deviation from 30°C. Values for β and E_s calculated based on the linear regressions are presented in Table 3, along with the fraction of first-year needle biomass for each of the collected samples. As seen in Table 3, emission factors were quite high for samples collected from the top and middle branches during June and early July for both years, and they began to decline in mid-July. This trend was not evident in samples collected from the lower branches. In both 1997 and 1998, the samples collected in September from the lower branches of the Douglas-fir had extremely high β and E_s values. In general, correlations were good until the end of the season in 1998 when E_s values were quite low. Because of the relatively limited number of samples collected in each year, the data do not support the examination of year-to-year differences.

3.3. Emissions as a function of canopy height

Previous research has shown that isoprene emissions vary depending on location in the canopy. Sunlit leaves at the top of the canopy have higher standard emission factors than leaves located in the shady lower portion of the canopy (Harley et al., 1996). Very little research has focused on the branch-to-branch variability of monoterpene emissions, or the emissions as a function of crown position (height). Bertin et al. (1997) reported high variations of standard monoterpene emissions (differences of 1 order of magnitude) between sun-exposed branches and shade-adapted branches of *Quercus ilex*, and both Guenther et al. (1991) and Komenda and Koppmann (2002) found large variations in leaf-to-leaf and branch-to-branch monoterpene emissions from *Eucalyptus globulus* and Scots Pine (*Pinus sylvestris*), respectively. Based on samples collected from sun-exposed and shade-adapted branches in this study, there does appear to be a significant difference in the standard emission factor and the temperature dependence factor at different heights (growth environments) within the canopy for western hemlock, but not for Douglas-fir. Table 3 (bottom) presents all of the enclosure samples sorted by sunlit (samples from the top branches and from the south side of the tree) versus shady (samples from the middle and the bottom of the crown) growth environment. Although there is significant scatter among the data (typical R^2 values range from 0.3 to 0.4), there is remarkable consistency in the Douglas-fir regression coefficients (β and E_s). The hemlock samples, in contrast, have widely varying regression coefficients, and, in general, the emissions show very little exponential increase in emissions with increasing temperature. This is also evident with the very low correlation coefficient ($R^2 = 0.04$).

4. Air quality impact of measured emissions

Photochemical models used to predict tropospheric O_3 concentrations, particulate matter (PM), and other atmospheric pollutants require accurate estimates of

Table 3
Standard emission factors (E_s in $\mu g\,C\,g^{-1}\,h^{-1}$) and temperature-dependence parameters β ($^{\circ}C^{-1}$) for the sum of all monoterpenes from Douglas-fir samples at each branch during each field campaign, and for sunlit vs. shaded branches

	E_s	β	R^2 (n)	f	Avg temp
Top branch					
2 July 1997	1.75	0.16	0.66 (3)	0.33[a]	26.1±3.2
15 July 1997	0.92	0.05	0.42 (3)	0.33[a]	22.5±3.5
10, 11 September 1997	0.26	0.08	0.88 (4)	0.65[b]	22.1±2.1
29 June 1998	2.22	0.22	0.90 (3)	0.51[c], 0.65[b]	26.5±6.0
27, 29 July 1998	0.31	0.23	0.65 (10)	0.51[c], 0.65[b]	31.7±5.5
18, 19 August 1998	0.10	0.06	0.14 (11)	0.51[c], 0.65[b]	24.5±3.7
10 September 1998	0.07	0.02	0.01 (7)	0.51[c], 0.65[b]	25.6±2.8
Middle branch					
4 June 1997	2.69	0.20	NA (2)	0.38[a]	17.0±4.5
2 July 1997	1.89	0.19	0.86 (3)	0.38[a]	26.6±3.6
15 July 1997	1.72	0.10	NA (2)	0.38[a]	25.3±3.9
10, 11 September 1997	0.15	0.05	0.41 (4)	0.76[b]	22.5±2.3
27, 29 July 1998	0.23	0.22	0.99 (8)	0.50[c], 0.76[b]	32.9±6.9
18, 19 August 1998	0.14	0.17	0.59 (8)	0.50[c], 0.76[b]	24.9±4.0
10 September 1998	0.16	0.12	0.64 (4)	0.50[c], 0.76[b]	28.6±3.0
Lower branch					
2 July 1997	1.38	0.09*	NA (1)	0.29[a]	22.7
15 July 1997	1.71	0.08	NA (2)	0.29[a]	26.1±7.0
10, 11 September 1997	3.21	0.43	0.78 (4)	0.55[b]	22.5±2.1
29 June 1998	0.88	0.03	0 (3)	0.43[c], 0.76[b]	34.0±0.3
27, 29 July 1998	0.15	0.20	0.88 (6)	0.43[c], 0.76[b]	30.7±7.0
18 August 1998	0.22	0.30	0.45 (4)	0.43[c], 0.76[b]	26.0±3.9
10 September 1998	4.08	2.39	0.62 (4)	0.43[c], 0.76[b]	27.9±0.1
Douglas-fir all (1997–1998)					
Sunlit branches	0.30	0.15	0.30 (51)	Top branches	26.2±4.7
Shaded branches	0.29	0.15	0.38 (55)	Middle/lower	27.2±5.9
Western hemlock (1997–1998)					
Sunlit branches	1.35	0.10	0.40 (28)	Top branches	25.6±6.5
Shaded branches	0.75	0.03	0.04 (61)	Middle/lower	27.0±6.9

R^2 is the correlation coefficient, n the number of enclosure samples collected, f the fraction of first-year needle biomass in the enclosure, Avg temp the average needle temperature within the enclosure±one standard deviation, and the letters a, b, and c denote the type of enclosure used: a is LiCor 6200, b is LiCor 6400, and c is Teflon bag. Where only one sample was collected, the default value of $\beta = 0.09\,^{\circ}C^{-1}$ was assumed.

biogenic emissions. Hanna et al. (2001) showed that for the UAM-V photochemical model, biogenic VOCs ranked 6th out of 128 input variables that have significant correlations with predicted ozone concentrations. The questions posed by this study were what is the sensitivity of a canopy-type biogenic model, such as the global biosphere emissions and interactions system (GLOBEIS), to changes in the standard emission factors? Furthermore, what is the sensitivity of a photochemical model such as the community multi-scale air quality model (CMAQ) (US Environmental Protection Agency, 1999) to uncertainties in the biogenic emission inventory?

The modeling system was comprised of the mesoscale meteorological model version 5 (MM5), a gridded anthropogenic emission inventory compiled from the EPA 1996 national emission inventory using the sparse matrix operating kernel emissions (SMOKE) processor, the GLOBEIS BVOC emissions model (driven with MM5 meteorological fields) and the CMAQ model. A 375×735 km domain with 5 km grid resolution covering the PNW (northern Oregon up to and including part of Canada, and eastward to the Cascade Mountains in WA) was selected and modeled for 11–14 July 1996. This domain and period were the basis for a number of previous air quality simulation studies we have

conducted to improve our understanding of regional air quality in the Pacific Northwest (Barna et al., 2000; O'Neill, 2002).

Total BVOC emissions for this domain were estimated using GLOBEIS (Guenther et al., 2000), which is a canopy model similar to the current US Environmental Protection Agency (USEPA) regulatory model BEIS3 (Geron et al., 1994; Pierce et al., 1998). The photochemical model CMAQ (US Environmental Protection Agency, 1999) was used to explore the changes in O_3 and SOAs as a result of altering biogenic emissions. CMAQ is a three-dimensional Eulerian grid model with aerosol chemistry and dynamics (Byun and Ching, 1999). The RADM2 gas-phase mechanism with aqueous chemistry and aerosol dynamics was used in this application.

In the PNW, forested areas account for 55% of the land surface area, with Douglas-fir and western hemlock accounting for 61% of the species in those forests. In the Cascadia airshed, biogenic emissions account for 91% of the total VOC loading, with monoterpenes accounting for 37% of the total VOC loading. The modeling system was run twice with different inputs. For the initial case, BEIS3 emission factors were selected since they are currently the regulatory standard. BEIS3 emission factors for Douglas-fir and western hemlock are 1.6 and 0.2 $\mu g\,C\,g^{-1}\,h^{-1}$, respectively, and for monoterpene emissions a temperature dependence factor of $\beta = 0.09°C^{-1}$ is assumed. The second case was modeled by adjusting only the Douglas-fir and western hemlock emission factors to the average emission factors as measured in this study. Both years of enclosure samples were used to determine one average emission factor for each species, and a slightly higher temperature dependence factor ($\beta = 0.10°C^{-1}$) was also used. Thus, for Douglas-fir and western hemlock, E_s values of 0.39 and 0.95 $\mu g\,C\,g^{-1}\,h^{-1}$ were used. This equates to a 76% decrease in the Douglas-fir emission rate, but an increase in the western hemlock emission rate by a factor of 4.75.

Results from GLOBEIS indicate that applying the revised emission factors to the PNW domain yields a decrease in total monoterpene emissions, as shown in Fig. 1. The figure on the left presents the emissions in moles per second ($mol\,s^{-1}$) for all monoterpene compounds using the BEIS3 regulatory emission factors. The figure on the right shows the difference in the GLOBEIS output between case 2 (using measured emission factors from this study) and the base case (using current regulatory emission factors). For both cases, peak monoterpene emissions occurred in southern WA on 13 July at 15:00 PST, with base case peak emissions estimated at 1.29 $moles\,s^{-1}\,grid^{-1}$, and case 2 emissions at 1.23 $mol\,s^{-1}\,grid^{-1}$, for a decrease of 5%. However, the greatest areal extents of changes in emissions appear in western WA and OR as identified in Fig. 1. Comparing emissions from the smaller domains (areas 1 and 2) centered along the WA/OR border for 13 July at 15:00 PST, average monoterpene emissions were decreased by 12% and 18% for areas 1 and 2, respectively. Overall the domain wide average of all monoterpene emissions during the entire modeling period changed by −19% between the base case and case 2.

In order to test the sensitivity of O_3 and aerosol formation to changes in biogenic emissions, the revised biogenic emission inventory (GLOBEIS output) was

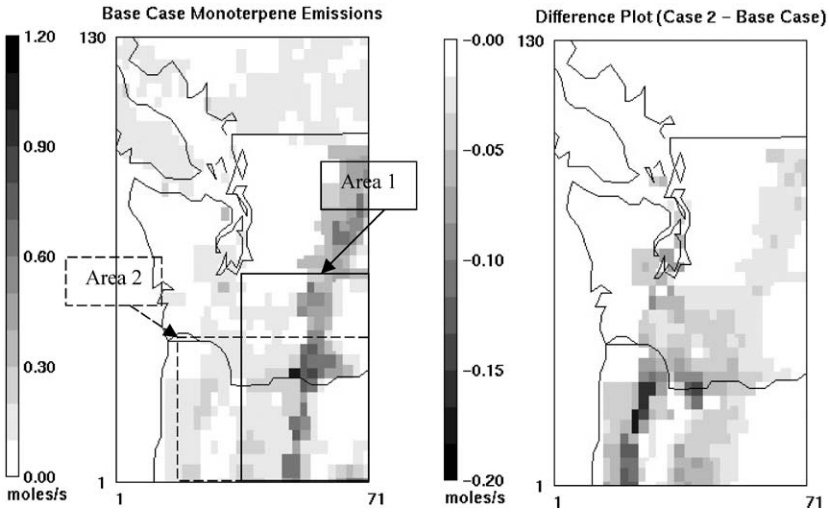

Fig. 1. Monoterpene emissions estimated using GLOBEIS for 13 July 1996 at 15:00 PST in $mol\,s^{-1}$. Base case using BEIS3 regulatory emission factors, and the difference in emissions between the base case and case 2 using measured emission factors from this study of Douglas-fir $E_s = 0.39$ and western hemlock $E_s = 0.95$ and $\beta = 0.1°C^{-1}$. Area 1 average emissions decreased by 12% during the peak emission period while area 2 emissions decreased by 18%.

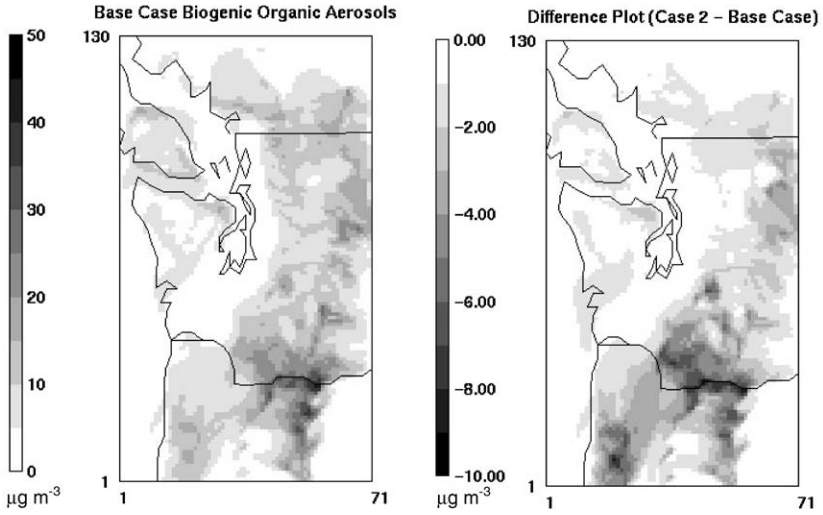

Fig. 2. Secondary biogenic organic aerosols estimated by CMAQ for 14 July 1996 at 8:00 PST in $\mu g\,m^{-3}$. Base case shown on the left and the difference between the base case and case 2 presented in the right graphic. Area 1 estimated aerosols decreased by 20% during the peak aerosol period while area 2 aerosols decreased by 24%.

used as input to CMAQ. Results from the CMAQ model are shown in Fig. 2, with the peak organic aerosol concentration shown in the figure on the left and the difference between the base case and case 2 shown on the right. The peak aerosol concentration occurred 14 July, at 8:00 PST with the base case concentration estimated at $42\,\mu g\,m^{-3}$ compared to an aerosol estimate of $34\,\mu g\,m^{-3}$ (−19% change) for case 2. Differences in average aerosol concentrations for the entire domain, area 1 and area 2 were fairly similar to each other, ranging from −20% to −24%. The largest difference between the two cases occurred on 13 July, 8:00 PST when the difference at one grid point was −46%. The O_3 production in the PNW estimated by CMAQ did not change significantly with the revised biogenic emission inventory. Peak O_3 levels were estimated to be 117 and 116 ppbV for the base case and case 2, respectively. The greatest difference in O_3 levels (−6%) was correlated with the time and location of the greatest difference in SOA concentrations.

Previous modeling work done for the PNW (Jiang et al., 2003; Barna et al., 2001; Chen, 2002) involved sensitivity analyses to investigate how reductions in VOC/NO_x emissions effect O_3 production. Barna et al. (2001) reported that just reducing anthropogenic VOCs alone results in a linear reduction in peak O_3 concentration, with each 1% decrease in VOC emissions yielding a 0.3–0.4 ppb drop in the 1-h peak ozone level. Results from this study show a 1% decrease in monoterpene emissions yields a 0.06 ppb drop in the 1-h peak ozone level. If one considers that monoterpenes account for about 20% of the effect of total biogenic emissions on peak ozone formation (Jiang, 2001), and that revisions to the biogenic emission inventory for this study were only for monoterpenes, then results between the two studies compare quite favorably. Chen (2002) reported that PM with a diameter $<2.5\,\mu m$ (PM2.5) changed linearly with changes in VOC emissions at multiple monitoring sites; however, various sites had different degrees of aerosol sensitivity. The aerosol sensitivity is a measure of the change in PM2.5 per unit percentage change in precursor VOC emissions. The aerosol sensitivity to changes in biogenic VOCs as reported by Chen (2002) ranged from 0.6 to 8.0 ($\mu g\,m^{-3}$ PM2.5/%VOC emission change) for various sites within the PNW, and for this study the domain wide sensitivity was $1.2\,\mu g\,m^{-3}$ SOA/%VOC emission change. Domain wide average daily biogenic VOC emissions reported by Chen (2002) were 45.9 vs. $33.6\,kg\,km^{-2}$ for the base case and $29.3\,kg\,km^{-2}$ for case 2. In CMAQ chemistry, the monoterpenes have roughly twice the aerosol yield as other organic gases, so one would expect to see significant changes to the SOA concentrations after modifying the terpene emissions.

5. Conclusions

Biogenic hydrocarbons are important inputs into photochemical models that are used to simulate air quality. Biogenic emission inventories are currently developed using simple canopy models that rely on species-specific standard emission factors and various correction terms to account for differences in environmental conditions, such as temperature and light. Enclosure samples were collected from two species,

Douglas-fir and western hemlock during the growing season over 2 years. Samples were collected from branches at various heights from 13 to 51 m within the canopy (different growth environments), and emission rates were standardized to 30°C using the Guenther emission algorithm (Guenther et al., 1993).

Emission rates were highly variable over the 2 years ranging from $0.01\,\mu g\,C\,g^{-1}\,h^{-1}$ at temperatures around 14°C to a maximum of $6.26\,\mu g\,C\,g^{-1}\,h^{-1}$ measured at 42°C. Even when standardized to 30°C, there was substantial scatter in the data making it difficult to identify any seasonal or annual trends. Standardized emission rates from this study for Douglas-fir are 76% less than current regulatory emission rates and western hemlock emission rates are greater by a factor of 4.75. During the course of both summers, there appears to be a general decline in standard emission factors for the Douglas-fir, but no seasonal trend for the hemlock. For Douglas-fir there is no significant difference in standard emission factors (E_s) or temperature dependence parameters (β) as a function of sunlit versus shaded growth environment. For hemlock, samples from the sunlit portion of the crown show typical emission factors (i.e. emissions that are exponentially dependent on temperature), but shady emission samples have no exponential correlation with temperature.

GLOBEIS was used to estimate the PNW regional biogenic emission inventory based on measurements obtained during this study, and CMAQ was used to estimate the changes in O_3 and SOAs as a result of modifying the biogenic emission inventory. Using the measured standard emission rates from this study for Douglas-fir and western hemlock species only, estimated biogenic emissions decreased across the PNW by 19% compared to BEIS3 standard estimates. The relatively small difference in biogenic emissions is slightly misleading, as the difference in standard emission rates between this study and current regulatory rates is quite significant, and they offset each other when combined in this domain. Ozone production as a result of the changed biogenic emissions did not change significantly; however, there was a significant change in the SOA concentration. Estimated aerosol concentrations decreased across the PNW by 20%, and in the southern section of the domain, differences in aerosol concentration peaked at −24%. Thus, accurately determining the biogenic emission inventory is important for predicting secondary pollutants such as PM 2.5.

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