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Approaches for quantifying reactive and low-volatility biogenic organic compound emissions by vegetation enclosure techniques – Part B: Applications

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ABSTRACT

The focus of the studies presented in the preceding companion paper (Part A: Review) and here (Part B: Applications) is on defining representative emission rates from vegetation for determining the roles of biogenic volatile organic compound (BVOC) emissions in atmospheric chemistry and aerosol processes. The review of previously published procedures for identifying and quantifying BVOC emissions has revealed a wide variety of experimental methods used by various researchers. Experimental details become increasingly critical for quantitative emission measurements of low volatility monoterpenes (MT) and sesquiterpenes (SQT). These compounds are prone to be lost inadvertently by uptake to materials in contact with the sample air or by reactions with atmospheric oxidants. These losses become more prominent with higher molecular weight compounds, potentially leading to an underestimation of their emission rates. We present MT and SQT emission rate data from numerous experiments that include 23 deciduous tree species, 14 coniferous tree species, 8 crops, and 2 shrubs. These data indicate total, normalized (30 °C) basal emission rates from <10 to 5600 ngC g^{-1} h^{-1} for MT, and from <10 to 1150 ngC g^{-1} h^{-1} for SQT compounds. Both MT and SQT emissions have exponential dependencies on temperature (i.e. rates are proportional to $e^{\beta T}$). The inter-quartile range of β-values for MT was between 0.12 and 0.17 K^{-1}, which is higher than the value commonly used in models (0.09 K^{-1}). However many of the MT emissions also exhibited light dependencies, making it difficult to separate light and temperature influences. The primary light-dependent MT was ocimene, whose emissions were up to a factor of 10 higher than light-independent MT emissions. The inner-quartile range of β-values for SQT was between 0.15 and 0.21 K^{-1}.

1. Introduction

Biogenic volatile organic compound (BVOC) emissions and quantitative descriptions of their landscape fluxes have and continue to garner much interest by atmospheric chemists and modelers as these compounds play important roles in tropospheric oxidation and aerosol chemistry. Micrometeorological flux measurements of low volatility and highly-reactive BVOC have eluded researchers due to many measurement challenges. Therefore, emission measurements by vegetation enclosure techniques have proven to be a viable alternative approach for assessing these BVOC emission rates. Previous research publications and constraints in these emission studies were reviewed in the preceding companion paper (Ortega and Helmig, 2008) to this publication. We now present examples of recommended experimental approaches aimed at quantifying low volatility and highly reactive BVOC and associated data from a number of emission experiments. In addition, we discuss experimental precision and BVOC recovery rates to demonstrate some of the analytical limitations in this research and present guidelines that should result in better comparability of quantitative emission data.

2. Applications of enclosure techniques for monoterpene and sesquiterpene emission studies

The following sections describe specific materials and experimental details that were found effective for measurements of low volatility and highly reactive BVOC (i.e. monoterpenes (MT) and sesquiterpenes (SQT)) from vegetation enclosures. Other materials from different manufacturers can and have been used by other researchers with equally effective results. The critical point of these descriptions is that, though these are not the only available methods, they conform to recommendations for achieving quantitative MT and SQT emissions data that were presented in the preceding review.

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2.1. Volume, residence time, flow rate and design of enclosure systems

Fig. 1 shows a schematic of the critical components of the dynamic branch enclosure system that was used in this research to quantify BVOC emissions with a specific emphasis on reactive MT and SQT. We chose the branch enclosure system as this method has a number of advantages over alternative techniques (e.g. leaf cuvettes or growth chambers) in terms of amount of biomass to be enclosed, the ability to average over many leaves, and for achieving a low residence time but high enough concentration of BVOC for sensitive chemical analysis. The 30–50 l enclosure volume was generally adequate to meet several critical sampling and analytical criteria. First, a sufficient amount of leaf biomass (10–30 g dry weight) was enclosed such that the resulting emissions created BVOC mixing ratios, which were within a range that allowed for relatively high time resolution (~hourly) collection of samples (using solid-adsorbent sampling and analysis via thermodesorption gas chromatography (GC)). Second, this enclosure volume was large enough for the bag to be suspended around part or most of a typical tree branch without touching the leaves. Two types of enclosure systems (using either Teflon or Tedlar bags) were employed. Advantages of these materials were discussed in the preceding companion paper (Ortega and Helmig, 2008). The first enclosure type included a cylindrical Teflon bag with two open ends, in which one end was sealed around the trunk side of a branch. The other end was placed around an elliptical Teflon base (20 × 15 cm, 1.2 cm thick) and was supported by an adjustable tripod. Two bulkhead tube fittings were attached to the base; one for the purge air inlet and the other for drawing samples. A DC motor was mounted to the outside of the Teflon base with the shaft extending into the enclosure. An aluminum fan blade (8 cm diameter) was fastened to the shaft and rotated at ~100 rpm to mix the enclosure air. The second type of enclosure was composed of a rectangular Tedlar bag (Jensen Inert Products, Part no. GST002S-2436TJC, Coral Springs, Fl) with one open end and two ports (with 6.3 mm tube fittings), again for the purge air and sampling lines. A picture of this type of enclosure is shown in Fig. 2. Before enclosing a branch with this second type of enclosure, two rings of rigid tubing were fastened to the outside of the enclosure to minimize the contact of the bag with foliage. Bags were then carefully placed over branches. Nylon cable ties were used to tightly secure the open ends around the trunk side of the branches. After the enclosure filled with purge air, the outside rings were removed, and the positive air pressure inside the bag maintained the shape of the enclosure. Excess air supplied to the enclosure was allowed to escape through the open side of the bag (the side secured to the branch). The enclosure was suspended from higher branches or other supports using thin (~28 gauge) wire. This helped to keep the enclosure upright, minimize contact with the enclosed foliage, and enabled the branch and enclosure to move with the wind as a

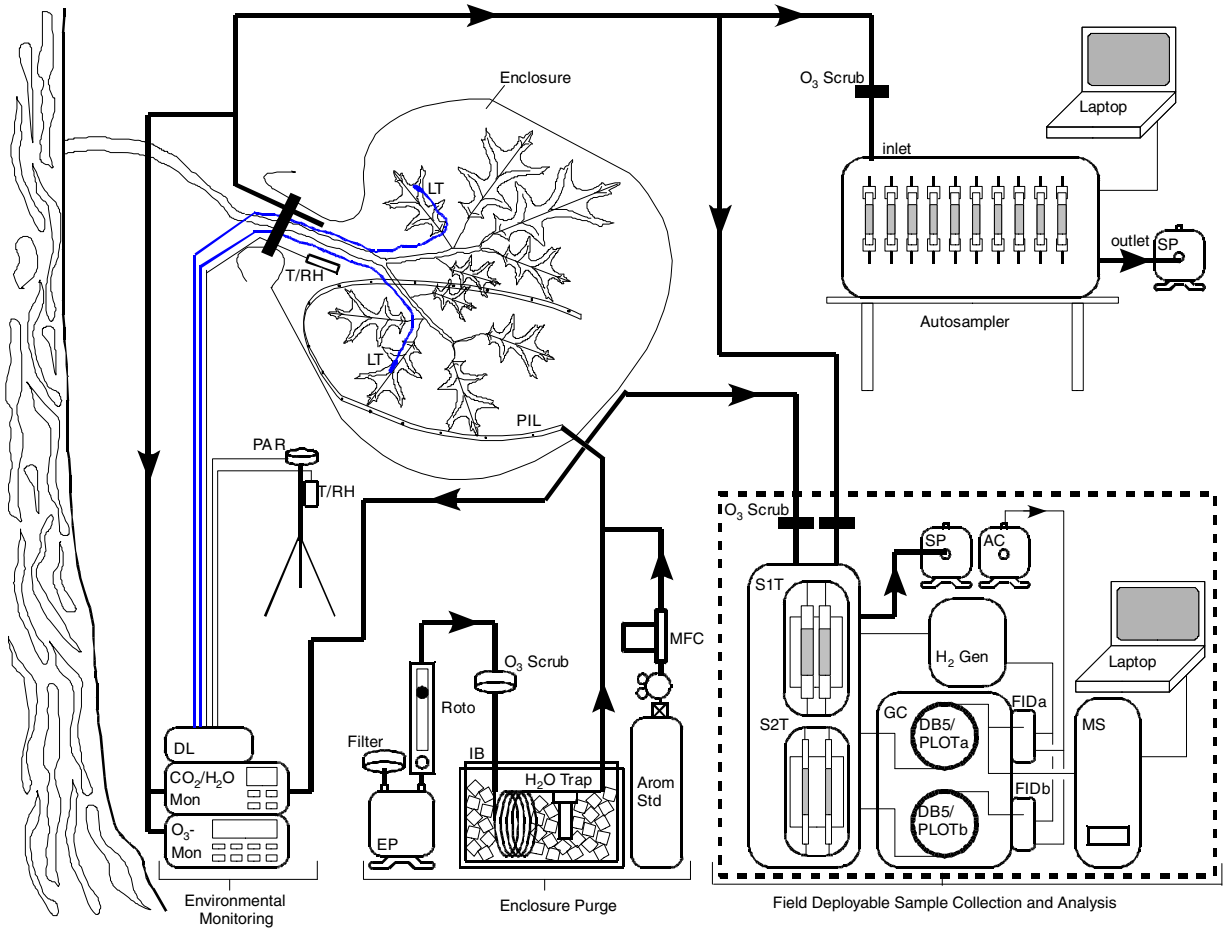

Fig. 1. Branch enclosure and associated apparatus. Symbols are as follows: LT = leaf temperature thermocouple, T/RH = temperature and relative humidity probe, PIL = perforated inlet line, PAR = light sensor, Arom Std = aromatics standard cylinder, MFC = mass flow controller, DL = datalogger, O_3-Mon = ozone monitor, CO_2/H_2O Mon = infrared gas analyzer (IRGA) for monitoring branch photosynthesis and transpiration, Roto = rotometer, EP = enclosure pump, SP = sampling pump, O_3 scrub = ozone scrubbers, IB = ice bath, H_2O trap = water trap, S1T = 1st stage traps, S2T = 2nd stage traps, GC = gas chromatograph, H_2 Gen = hydrogen generator, FID = flame ionization detector, DB5/PLOT = chromatography columns, MS = mass spectrometer. Dashed rectangle (at lower right) indicates critical components of the Field-GC. Certain valves, heaters, electronics, and other components have been excluded for clarity.

Fig. 2. Photograph of a branch enclosure on a loblolly pine tree at Duke Forest, NC (August 2005). The bag was made of 5-mil Tedlar, which was found to be 90–95% transparent to PAR. The enclosure was externally supported so that it did not touch the needles, and relatively air tight, which created a slight positive pressure inside the bag.

single unit. Great care was taken not to bend or break any leaves or needles on the branch. The tubing carrying the purge air extended through the fitting (into the enclosure) and was perforated to help distribute the air uniformly around the branch.

Branches were allowed to acclimate for 24 h (while purging the enclosure) before BVOC sampling began. Samples were collected from the enclosure air, concentrated onto solid-adsorbent cartridges (described below) with an autosampler (shown in the upper right part of Fig. 1) and analyzed by GC. Samples were also taken by an automatic sampling/GC system represented by the dashed rectangle in the lower right of Fig. 1. This system (further described in Section 2.6) was specifically designed for on-site and 24-h sample collection and analysis and was used as an alternative technique to the sample collection on cartridges.

2.2. Enclosure purge air

Purge air was provided by a high capacity (55 l min^{-1}) oil-free pump (Medo Corporation, Hanover Park, IL) equipped with an in-line particle/charcoal filter (Mersorb Part no. 463532; Mine Safety Appliances Company, Pittsburgh, PA) on the inlet to prevent particles and ambient hydrocarbons from entering the purge line. This charcoal filter had a low flow resistance, and had the added benefit of reducing ozone in the purge air to less than ~5 ppbv. A mass flow controller was used to control and to monitor the purge flow, typically between 10 and 20 l^{-1} min for a 50–100 l enclosure. At the beginning and end of the experiment, the purge air flow rate was calibrated using a volumetric flow meter (DC-Lite, BIOS International Corporation, Butler, NJ). This is an important measurement since the uncertainty in the purge flow translates directly into uncertainty in calculated emission rates (see companion paper, Eq. (1)). After the enclosure was in place, any other disruptions to the experiment were avoided to ensure that steady-state conditions were maintained. To further remove ozone, a customized commercial scrubber composed of 25 MnO_2-coated copper screens (O.B.E. Corp. Fredericksburg, TX) was placed on the pump outlet. Ozone in the purge air was regularly measured (Thermo Electron 49C ozone monitor, Franklin, MA) to monitor the efficiency of ozone mitigation. Air was cooled and dried prior to entering the enclosure by submerging a coiled section of copper tubing (6.3 mm O.D., 1 m length) into an ice water bath. The condensed water in the purge air stream was then collected and removed downstream in a water trap equipped with a drain nut (Balston type A912-BX, Balston Filter Products, Lexington, MA).

2.3. Environmental monitoring

Several environmental variables were recorded with a data logger (e.g. Model CR-10X or CR-23X; Campbell Scientific Corp., Logan, UT). These measurements included air and leaf temperatures (outside and inside the enclosure), relative humidity inside the enclosure, photosynthetically active radiation (PAR; 400–700 nm), and ambient ozone concentration. Leaf and ambient air temperatures were measured inside the enclosure using Teflon-sheathed type-K thermocouple wires (30 gauge; Omega Engineering, Stamford, CT). Thermocouples inside the enclosure were attached to the abaxial surfaces of selected leaves using porous medical tape (Transpore™, 3M Corporation, St. Paul, MN). Air temperature and relative humidity were measured inside the enclosure using a shaded HMP50 probe (Campbell Scientific, Logan, UT). PAR was measured using a quantum sensor (SB 190, LI-COR, Lincoln, NE). Net photosynthesis was calculated by monitoring inlet and outlet CO_2 concentrations with a LI-COR 6400 photosynthesis system and then scaling the difference of these concentrations to the measured leaf area and purge air flow.

2.4. Sample collection and analysis

A continuous air flow of 400–500 ml min^{-1} was drawn through the sampling lines from the enclosure. A fraction of this flow (~50%) was then periodically collected on adsorbent cartridges using either a 10-cartridge autosampler (Helmig et al., 2004a) or the field-deployable GC (Field-GC) described below. Flow rates were set to achieve turbulent flow within the sampling lines (to ensure adequate air mixing and minimal wall losses). Sampling rates onto the adsorbent cartridges (8.8 cm length × 6.3 mm OD) were typically set to 150–250 ml min^{-1}. The autosampler could be programmed to take samples at specified intervals with user-chosen parameters (such as sample duration, flow rate, number of samples, and timing). Typical sample volumes were 8–12 l for MT and SQT, and 200–500 ml for isoprene quantification. The adsorbent sampling temperature was kept at 40 °C (which was above the enclosure temperature) to prevent water accumulation on the adsorbent bed (Karbiwnyk et al., 2002). Tubes were periodically collected in series to check that sampling conditions did not result in analyte breakthrough. Samples collected on adsorbent cartridges were taken to the laboratory for analysis on an automated cartridge desorber (Model ATD 400, Perkin–Elmer, Waltham, MA) with GC separation and dual mass spectrometry (MS) and flame ionization detection (FID) as described in detail elsewhere (Helmig et al., 2004a; Pollmann et al., 2005). Compound identifications were achieved by comparison of retention times and mass spectra with literature data (Adam, 1989) and by comparison with results from authentic standards from a capillary diffusion system (Helmig et al., 2003). The FID signal was used for quantifying emissions using response factors that were derived from a well-characterized C_5–C_{16} hydrocarbon standard (Helmig et al., 2004b).

2.5. Reference standard

A quantitative internal standard composed of four aromatic compounds (toluene, 1,2,3,4-tetra-hydronaphthalene, 1,3,5-tri-*iso*propylbenzene, and *n*-nonylbenzene) was introduced into the bag purge air as shown in Fig. 1. There were three purposes for the addition of this standard: (1) To evaluate systematic losses of analytes of different volatility to the enclosure system (this objective can be accomplished by comparing inlet and outlet concentrations). (2) To provide an independent method of calculating emission rates (since the standard concentration and its dilution ratio was known, BVOC concentrations could be determined by a comparison to the resulting concentrations of the standard compounds). (3) To identify possible losses of biogenic emissions by foliage uptake (which can be accomplished by comparison of observed loss rates in using an empty bag with loss rates observed in an experiment with enclosed foliage).

The properties of this standard and its preparation method are listed in Supplemental Material section to this article. These non-biogenic aromatic compounds were carefully chosen to span a wide range of volatility ($\sim C_7$ to C_{15}), and to not interfere (i.e. co-elute) with the chromatography of target BVOC. Also, these compounds are relatively unreactive with respect to atmospheric oxidants and therefore any losses observed could primarily be attributed to deposition or uptake, and not due to chemical reactions. Using a flow rate of 5 ml min^{-1} of the reference standard (with the mixing ratios shown in Table 1 in the Supplemental Material section) into the bag purge flow ($\sim$10 l min^{-1}), a dilution factor of $\sim$2000 was achieved. The resulting mixing ratios were therefore $\sim$0.5 ppbv, which were similar in magnitude to typical BVOC concentrations in the enclosure (0.1–10 ppbv).

2.6. Field-GC

In addition to adsorbent cartridge sampling, a field-deployable analytical system was developed to perform sampling and real-time analysis of BVOC emissions in the field. A simplified drawing of this system is included in the lower right side of Fig. 1. Samples were trapped onto solid adsorbent-filled focusing traps, and analyzed by thermodesorption-GC. A key difference between this system and using a series of adsorbent cartridges is that the entire sampling and analysis process is always performed on the same set of adsorbent traps using a closed system, two-stage focusing process. This eliminates the need for handling, transport, and storage of samples to a laboratory (which can lead to analyte losses), as well as uncertainties associated with variability between different cartridges. The 2-channel GC-FID (Model 310C, SRI Instruments, Torrance, CA), the mass spectrometer (5973-MSD, Agilent Technologies, Palo Alto, CA) and all other components were enclosed in rigid weather-proof containers (Hardigg Industries, Inc., South Deerfield, MA) for continuous field use. The sample sequence, temperature control, valve switching and sample injection were all controlled by a custom LabView code using Field Point Modules from National Instruments (Austin, TX). Instrument control as well as the FID and MS data collection were accomplished by using laptop computers on site. The inlet system included four multi-port, two-position gas switching valves (Valco Instruments, Houston, TX) used to direct enclosure samples onto two sets of adsorbent traps. An additional 12-port, two-position valve was mounted inside the GC oven and provided the ability to select between two pairs of GC columns. The first two were CP-5 columns (Varian Chrompack; Length = 30 m, ID = 0.32 mm, 0.25 μm film), which were used for MT and SQT analysis. The second set was a pair of PLOT columns (Agilent technologies; Length = 25 m, ID = 0.32 mm; Al_2O_3/KCL, film thickness = 8.0 μm) and were used for isoprene analysis. A hydrogen generator (H2-50XR, SRI Instruments) with an external 1 l H_2 buffer reservoir was used to provide carrier gas and FID H_2. The system required a flow of approximately 40 ml min^{-1} of hydrogen, however during certain analytical steps, this flow was exceeded necessitating the buffer reservoir. Air was supplied to the FIDs by a compressor mounted inside the GC chassis.

The instrument collected two simultaneous samples, one from the inlet air and one from the enclosure air. It utilized a two-stage trapping and desorption process in which low concentrations ($\sim$1 ppbv) of analytes were initially collected from large air volumes ($\sim$10 l) onto the 1st-stage traps. These traps the were purged of air and heated as hydrogen transferred the analytes on to the 2nd-stage microtraps (which were kept at −10 °C). Next, these microtraps were rapidly heated as analytes were injected onto the columns. Using this type of two-stage system optimized the efficiency of chromatographic separation. Both the 1st-stage and 2nd-stage traps contained multi-stage adsorbent beds to analyze a greater range of volatility than is possible with a single adsorbent (Helmig and Greenberg, 1994). The 1st-stage traps were filled with a combination of Tenax GR and Carboxen 563 allowing for quantitative analysis of compounds spanning a volatility range from isoprene (C_5) to SQT (C_{15}). The 2nd-stage adsorbent traps were filled with Unibeads and Carboxen 563 and controlled to −10 °C using Peltier coolers during sample transfer. The samples were injected onto the GC columns by switching the injection valve and rapidly heating the 2nd-stage traps from −10 °C to 300 °C in approximately 15 s while using H_2 as the purge and carrier gas. Approximately 10% of the GC column flow from the enclosure outlet sample ($\sim$0.5 ml min^{-1}) was directed into the MS. Therefore, for every sample pair that was taken from the enclosure, there were two FID chromatograms (one inlet and one outlet sample) and one MS chromatogram (outlet sample). Peak identification was performed using a combination of retention indices and mass spectral data. Following sample injection, the H_2 flows through the focusing traps were reversed, and both sets of traps were baked out at 325 °C to condition them prior to subsequent sampling. All system transfer lines and valves were temperature-controlled to 175 °C to prevent adsorption losses of heavier BVOC (in particular SQT). During routine field use, the FIDs were calibrated by syringe injection of a 1000 ppm hydrocarbon standard (C_1–C_6 *n*-alkanes in He; Scott Specialty Gasses, Longmont, Co). Calibrations were also performed by analyzing standards that were loaded onto adsorbent cartridges and subsequently installed into the system (in place of the 1st stage traps) for analysis. These cartridges had known quantities of VOC loaded from a compressed gas standard containing C_5–C_{16} hydrocarbons. These tests were used to ensure that heavier compounds were quantitatively transmitted through the system. Emission rates determined from the Field-GC system were in agreement with those determined using autosampler cartridges analyzed on the laboratory GC (Helmig et al., 2007).

2.7. Field site and sampling details

BVOC emission studies using the above detailed systems were conducted at several locations during the 2004–2006 growing seasons. Data presented here are from enclosure experiments performed in a mixed northern hardwood forest at the University of Michigan Biological Station (UMBS, Pellston, MI), from within a loblolly pine (*Pinus taeda*) plantation (established in 1983) in the Blackwood division at the Duke Forest FACTS-1 site in North Carolina (Chapel Hill, NC), at several locations in Boulder, CO, and near Humboldt State University in Arcata, CA. Enclosures were allowed to equilibrate for 24 h prior to sampling and in most cases were left in place for 2–3 days to capture more than one diurnal cycle of BVOC emissions with respect to changing light and temperature conditions. BVOC samples were typically taken every hour during the day, and every 2–3 h at night.

3. Results and discussion

3.1. Leaf and air temperature

Temperature is one of the primary influences on biogenic emissions. Measuring a single temperature within an enclosure containing many leaves with different orientations and degrees of shading can be problematic. Fig. 3 shows an example of leaf and air temperatures, relative humidity, and PAR from a two-day enclosure experiment on a *Populus grandidentata* branch. Besides measurements from inside the enclosure, leaf and air temperatures were also measured outside of the enclosure to monitor the degree of greenhouse heating inside the bag. There were periods of clouds and full sunlight as indicated by the PAR readings and these changes in radiation had a strong influence on temperatures. For most of this two-day period, leaf temperatures (inside and outside the enclosure) agreed within 2–3 °C. Leaf temperatures outside the enclosure were generally lower than leaf and air temperature within the enclosure. During periods with full solar irradiance, the difference between the ambient and the enclosure air temperature ("Temp probe") were highly variable and were as much as 8 °C for short periods, illustrating the effect of greenhouse heating inside the enclosure. Typical experiments were done with five temperature measurements to monitor temperature conditions and differences between enclosure foliage and leafs or needles outside of the enclosure. These included two leaf and one air temperature measurement inside the enclosure, and one leaf temperature and ambient air temperature outside of the enclosure. For clarity, only three of the temperature measurements are shown in Fig. 3. These measurements show that it is not uncommon for sun-lit leaf temperatures to be higher than the ambient temperature. Because of transpiration cooling, shade leaves can be lower than the ambient temperature. The enclosure air temperature measured with the temperature/relative humidity probe represents the average of sun-lit and shade leaves. This was deemed the most representative temperature for correlating emissions with temperature, for scaling emissions to whole-canopy fluxes, and for comparing multiple enclosure experiments.

3.2. Effect of transpiration

In order to counteract the solar heating and the buildup of excessive water inside the enclosure, purge air was typically cooled and dried using a water trap placed in an ice bath. The upper portion of Fig. 3 shows how relative humidity (%RH) inside the enclosure can be affected by varying temperatures and sunlight. The bag flow rate for this experiment was 16.2 l min^{-1}. On the first day, mid-day enclosure temperatures were generally 30–33 °C with a one-hour period (~17:00 h on day 206) between 38 and 40 °C. The following day, temperatures and light levels were significantly lower. The ice bath lowered the dewpoint of the incoming air to ~10 °C. Transpiration from the leaves added additional water to the enclosure resulting in relative humidity levels that were typically greater than 40% for all conditions. These RH levels were well within normal ambient conditions, under which the enclosed vegetation will typically show undisturbed physiological behavior. The enclosure purge air was not cooled and dried at night to the extent as it was during the day. With the lower nighttime transpiration rates from the leaves, lower air temperatures at night (typically 12–20 °C), and lack of incident radiation, resulting RH levels and temperatures inside the enclosure were always similar to ambient conditions.

3.3. Photosynthesis

Fig. 4 shows net photosynthesis (A_{net}) measurements from a loblolly pine (*Pinus taeda*) enclosure experiment. The mid-day values were within the range of light-saturated needle-level photo-

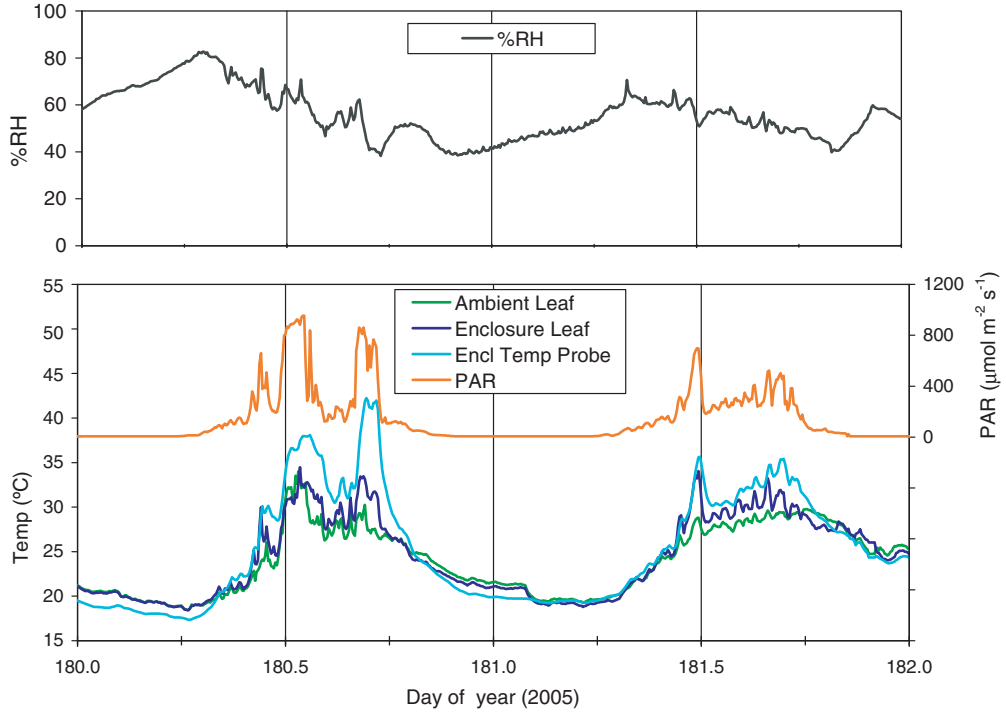

Fig. 3. Relative humidity, PAR, leaf temperatures, and temperature probe readings from a big tooth aspen (*Populus grandidentata*).enclosure experiment (June 29–30, 2005). "RH" is the relative humidity inside the enclosure. "Enclosure Leaf " is the temperature from the abaxial side of a leaf inside the enclosure, "Ambient Leaf" is the temperature of a leaf outside the enclosure, "Encl Temp Probe" is the air temperature inside the enclosure. PAR (photosynthetically active radiation) is the light level measured inside the enclosure through the Teflon film.

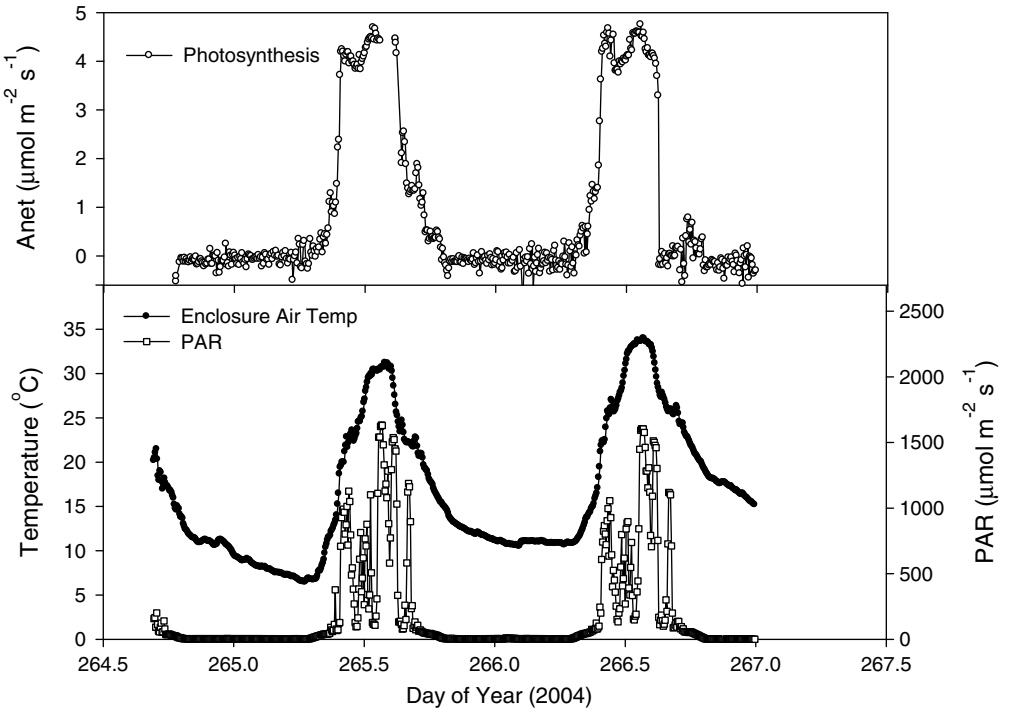

Fig. 4. Net photosynthesis (A_{net}), enclosure temperature and photosynthetically active radiation (PAR) measured on a sun-exposed loblolly pine (*Pinus taeda*) branch enclosure at Duke Forest, NC (September 21–22, 2004).

synthesis rates measured at the same site (Rogers and Ellsworth, 2002) and were reproducible on multiple days, which indicates that the enclosed branch was photosynthesizing normally. These photosynthesis and RH measurements demonstrate that the conditions during the experiments were typical of the plant's natural environment. Temperatures inside the enclosure were slightly higher than what ambient branches experienced during maximum solar irradiance, but not out of the normal range of ambient temperatures for that time of year (Herrick and Thomas, 2001).

3.4. Recovery rates of the internal standard

The four-component reference standard was introduced into the purge air flow (as described in Section 2.5) to study how compounds of varying volatility may be lost inside the enclosure. Concentration differences between the air going in and the air exiting the enclosure can be attributed to adsorption to internal surfaces of the experimental system or to the enclosed foliage. Fig. 5 shows two chromatograms from the outlet (top) and inlet (bottom) samples from a *Picea pungens* (blue spruce) enclosure experiment. The bottom chromatogram shows each of the four standard compound peaks, and the upper chromatogram shows these same peaks along with BVOC that were emitted by the branch. Mixing ratios and emission rates were calculated from the respective chromatogram peak areas from the inlet and outlet samples. The comparison of the concentrations of the different aromatic compounds provides an estimate of actual recoveries through the enclosure system and provides constraints on emission rate estimates. Fig. 6 shows a time series of the recovery rates for the series of aromatic compounds (outlet/inlet concentration ratios) from the same blue spruce enclosure. It is evident that the higher boiling point compounds (e.g. TIPB and NB) are not recovered to nearly the degree that more volatile compounds are. Fig. 7 shows the median ratios of all the aromatic compounds (from this same blue spruce experiment) as a function of compound boiling point. For comparison, the range of MT and SQT boiling points are included as horizontal bars. These data demonstrate that there can be substantial analyte losses and that loss rates increase for higher molecular weight compounds. Since MT and SQT fall within the volatility range of these aromatic test compounds, these findings emphasize the need to examine these effects and account for such losses when calculating and reporting BVOC emission rates from enclosure experiments. For example, the findings from this particular experiment suggest that measured MT and SQT emission rates can be substantially less than the actual emission rates, as the median losses indicated in Fig. 7 are on the order of 20–30% with an even greater range of losses (between 10–80%) observed in individual measurements.

3.5. Temperature response

Fig. 8 shows the sum of SQT emission rates as a function of temperature for a series of individual emission samples taken from a corn plant (*Zea mays var. rugosa*) enclosure. Modeled emission rates (*ER*) of light-independent MT and SQT assume a temperature-dependence of the form

$$\mathrm{ER(T)} = \mathrm{ER_0}[\exp \beta(T - T_S)], \quad (1)$$

where the predicted emission rate (ER(T)) at a given temperature (T) is a standardized emission rate (ER_0 typically at T_s = 303 K) multiplied by a scaling factor (β) that represents the exponential dependence on temperature (e.g. Guenther et al., 1995). The exponential regression fit of the SQT data in Fig. 8 yields a value of $\beta = 0.17\ K^{-1}$. Results from 20 different tree species that were investigated in these studies showed the SQT β-factor to have an average value of 0.17 K^{-1} with a range of 0.03–0.48 K^{-1}(inner-quartile range (IQR) = 0.15–0.21 K^{-1}). MT β-values ranged from 0.03–0.4 K^{-1} (IQR = 0.11–0.17 K^{-1}) with an average value of 0.14 K^{-1}. Atmospheric models generally assume a value of $\beta = 0.09\ K^{-1}$ for MT. Many of the MT results shown here also have a strong light dependence (see Section 3.6), which is difficult to separate from the temperature response in outdoor experiments. Since the light

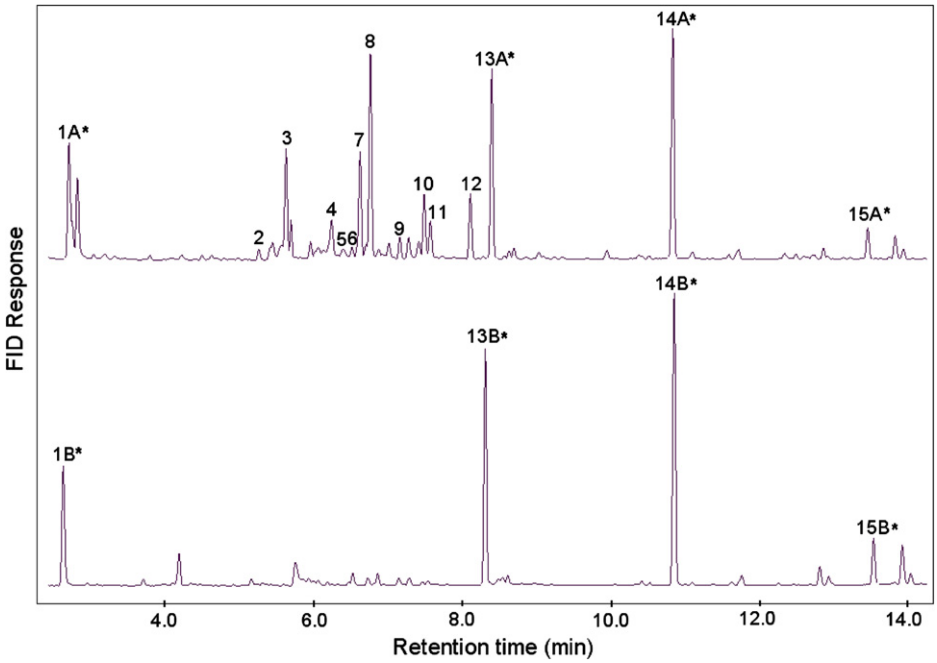

Fig. 5. Example FID chromatograms of outlet (upper) and inlet (lower) samples from a blue spruce (*Picea pungens*) enclosure. Both chromatograms are on the same scale. Peak identifications are as follows: 1A,1B: toluene, 2: α-pinene, 3: camphene, 4: β-pinene, 5: α-phellandrene, 6: δ-3-carene, 7: *o*-cymene, 8: *d*-limonene, 9: γ-terpinene, 10: *para*-cymenene, 11: terpinolene, 12: camphor, 13A, 13B: 1,2,3,4-tetra-hydronaphthalene, 14A,14B: 1,3,5-tri-*iso*-propylbenzene, and 15A, 15B: *n*-nonyl benzene. Compounds from the aromatic standard are indicated by an asterisk (*). Inlet channel peaks are designated "B".

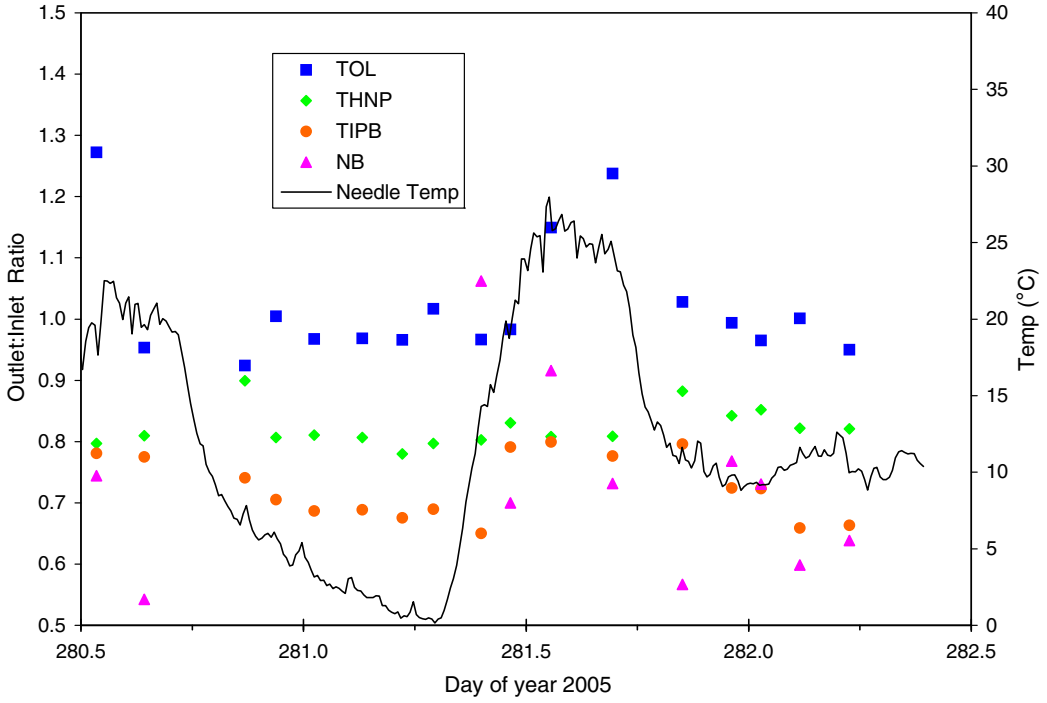

Fig. 6. Ratio of outlet:inlet concentrations of aromatic compounds introduced into a blue spruce (*Picea pungens*) enclosure in Boulder, CO and needle temperature measurements taken during this experiment. The compound abbreviations are as follows: toluene (TOL), 1,2,3,4-tetra-hydronaphthalene (THNP), 1,3,5-tri-*iso*-propylbenzene (TIPB), and *n*-nonylbenzene (NB).

dependency is not explicitly separated in Eq. (1), light-dependency of emissions will result in larger β-values in this type of regression analysis. Other studies have shown that there can be significant seasonal dependencies on β-values, which can lead to errors up to 130% in estimating canopy fluxes (Holzinger et al., 2006). The fact that SQT β-values were generally greater than MT β-values demon-

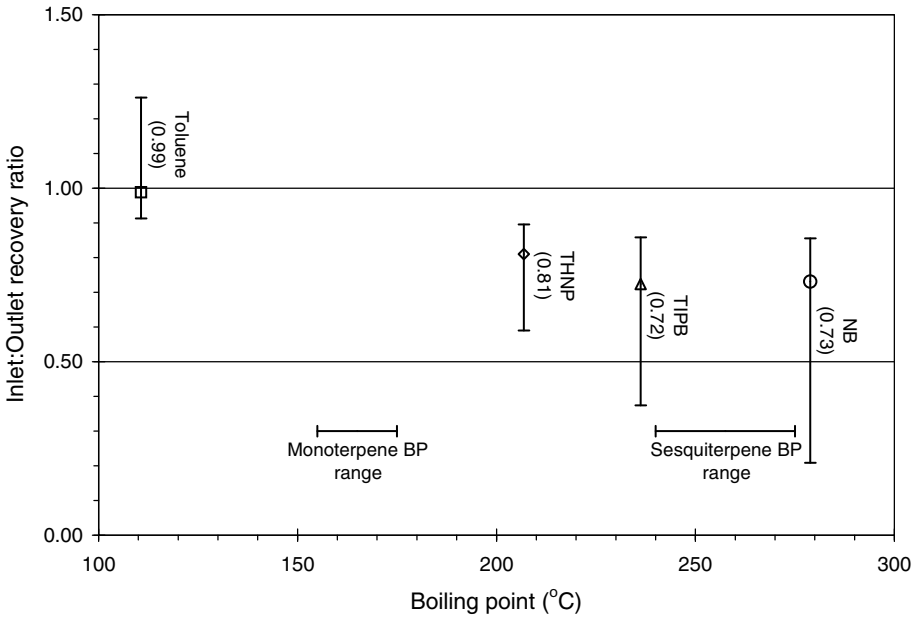

Fig. 7. Aromatic compound recovery ratios for the four internal standard compounds from 18 separate inlet and outlet sample pairs from a blue spruce (*Picea pungens*) experiment (Boulder, CO). This enclosure was kept in place for 2 days in October, 2005. Enclosure temperatures ranged from 1–33 °C. Points indicate median values, and error bars represent the entire data range of observed values.

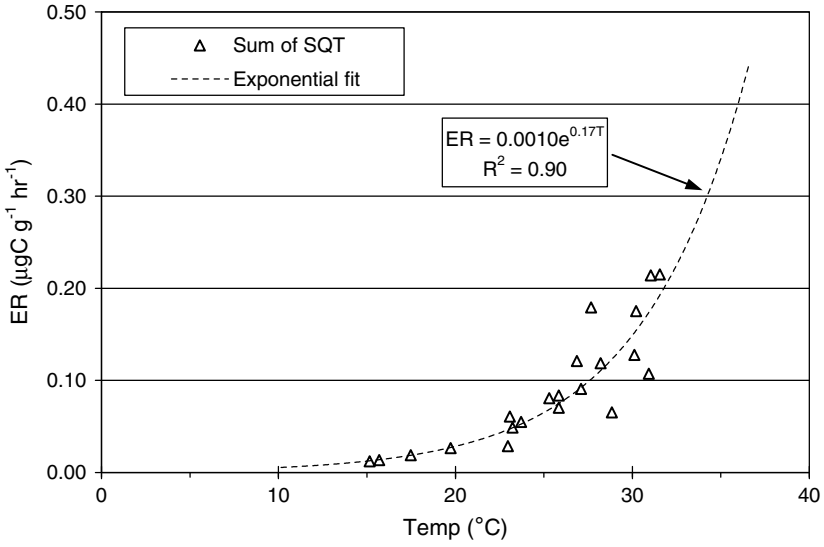

Fig. 8. Total sesquiterpene emission rate from a corn plant (*Zea mays* var. *rugosa*) in an enclosure experiment in Boulder, CO (August 19–23, 2006). Also shown is the best-fit exponential curve through the 21 data points indicating a β factor of 0.17 K^{-1}.

strates that SQT emissions become increasingly important in warm weather conditions ($T \geqslant 35$ °C), and that under such conditions SQT can possibly exceed MT emissions (Helmig et al., 2006).

3.6. Light-dependent monoterpene emission rates

Emissions of certain BVOC have been shown to be highly dependent on light (PAR). Fig. 9 shows as an example MT emissions from a two-day experiment on a red oak (*Quercus rubra*) tree. Light and temperature are also plotted with this time series data. Emissions of both *cis*- and *trans*-ocimene were negligible at night, and emission rates for both isomers increased during the day. But it is evident that the *trans*-isomer emissions were light-dependent as the *trans*-ocimene concentration increased greatly (by up to a factor of 10) and at a much higher rate than for the *cis*-isomer during full solar irradiation. For several hours during these two days, the environment during this experiment represented the warmest and most sunlit conditions that sunlight-exposed branches would likely experience. The resulting MT emission rates (dominated by *trans*-ocimene) were between 5 and 7 $\mu g\, C\, g^{-1}\, h^{-1}$ and appeared 1–2 h after temperature exceeded ~35 °C. Other experiments on tulip poplar, red maple, red oak and paper birch have shown similar results with light-dependent ocimene emission rates (between 5 and 10 $\mu g\, C\, g^{-1}\, h^{-1}$) (Table 1). These findings are in agreement

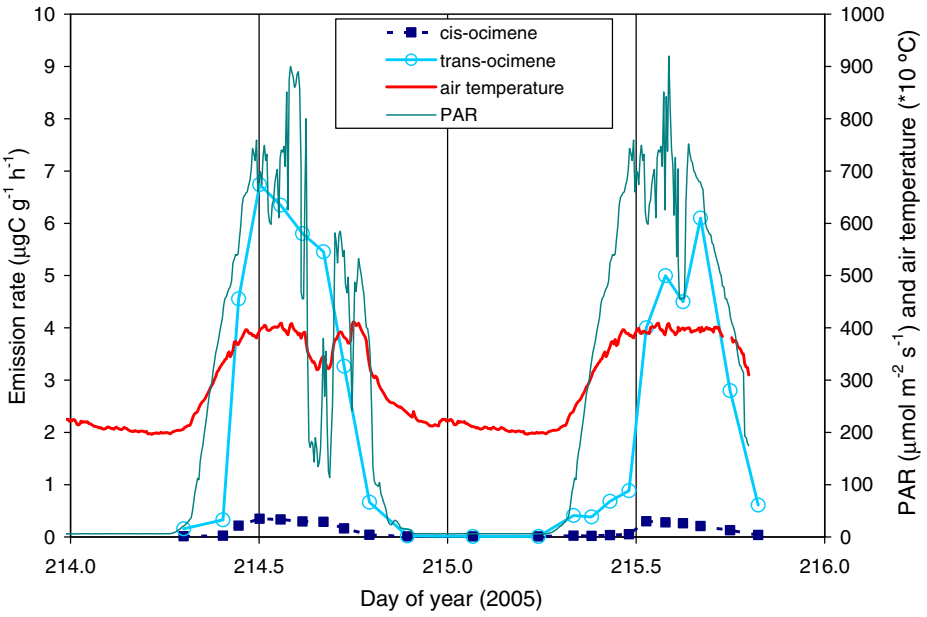

Fig. 9. Two days of environmental and monoterpene emission rate data from a red oak (*Quercus rubra*) enclosure at UMBS (July 2005). The air temperature in the enclosure was multiplied by 10 to display it on the right hand *y*-axis with PAR.

with results from other recent studies from Europe. Staudt et al. (2003) reported significant increases in ocimene emission rates from holm oak (*Quercus ilex*) that reached up to ~4 μg C g^{-1} h^{-1} 2–3 h after leaf temperature was increased from 25 to 35 °C. Similarly, Dindorf et al. (2006) and Holzke et al. (2006) reported light-dependent MT emissions (primarily sabinene) from European birch (*Fagus sylvatica*) over two growing seasons in Germany. Dindorf et al. (2006) further demonstrated the light-dependency of these emissions by removing the light during daytime experiments, which showed that emissions essentially ceased during these dark periods. They suggested that incorporating the large light-dependent MT birch-tree emissions into models would result in significant increases in predicted European BVOC budgets.

The growing evidence of light-dependant MT emissions from major tree species emphasizes the importance of considering this effect for assigning MT emission factors for certain forested regions. Both temperature and light dependencies need to be considered for the description of these emissions, with the caveat that for certain MT emissions from broadleaf species, a temperature threshold needs to be achieved for appreciable emissions to occur. More research is ongoing to further refine the light and temperature-dependency of these emissions with respect to MT speciation, vegetation type, light, temperature, and canopy position.

3.7. MT and SQT emission rate results from selected field studies

Experiments were performed on a variety of tree species, crops and shrubs at different field sites (see Section 2.7) to determine MT and SQT basal emission rates. A number of experiments were done on several branches or individual trees of the same species to better characterize variability of emissions. There were 13 individual coniferous tree species, 23 deciduous tree species, eight crops and two shrubs tested in the course of these studies. Great care was taken with all experimental procedures to minimize (and account for) depositional losses of low volatility compounds. Table 1 summarizes the basal emission rates and β-factors from these experiments. Please note that these values are the emission rates as determined from the experiment and that these data have not yet been corrected for the potential compound losses that were identified in the internal standard experiments. Consequently, these values should be considered as lower estimates with the likely possibility that these data (on average) are 10–30% lower than actual emissions. Other experimental details are also listed, such as the number of emission samples taken, maximum and minimum enclosure temperatures, and regression results (R^2) for β-factor calculations. The β-factors were determined by plotting the calculated emission rates against enclosure air temperature and fitting an exponential regression curve through the data points. The basal emission rate is defined at a temperature of 30 ° C. For experiments with a low number of data points or poor correlations, basal emission rates (ER_0) were calculated from the measured emission rates (using Eq. (1) in Section 3.5), with assumed β-factors of 0.10 K^{-1} for MT, and 0.17 K^{-1} for SQT. For these particular cases, the calculated basal emission rates in Table 1 are listed as means (with the standard deviation in parentheses) of available measurements. As previously mentioned, several deciduous species were shown to exhibit light-dependent MT emissions. In these cases, emission rates were first corrected to standard light conditions (PAR = 1000 μmol m^{-2} s^{-1}) by multiplying the calculated emission rates by a light correction factor (Guenther et al. (1991),

$$C_{PAR} = 1000\left[\frac{\sqrt{(1+(0.027*PAR)^2)}}{2.878*PAR}\right], \quad (2)$$

where PAR represents the measured light level for each emission sample.

The results show that there is a wide range of variability among emission rates for both MT and SQT. All tested conifer species showed MT emissions, and most exhibited SQT emissions as well. These emission rates ranged from 0.1 to 4.02 μg C g^{-1} h^{-1} and <0.01 to 0.62 μg C g^{-1} h^{-1} for MT and SQT, respectively. For comparison, the results from deciduous tree species were <0.1–4.78 μg C g^{-1} h^{-1} and <0.01–0.53 μg C g^{-1} h^{-1} for MT and SQT, respectively. The crops and shrubs that were tested had emission results more similar to the deciduous tree species. As previously

Table 1
Total monoterpene and sesquiterpene basal emission rates (BER) and temperature coefficients for observed temperature dependencies

Common name	Genus/species	No. of enclosures	Total number of samples	Enclosure temperature range (°C)	Total MT BER[a] ($\mu gC\ g^{-1}\ h^{-1}$)	β(MT) ($°C^{-1}$)	R^2(MT)	Total SQT BER[b] ($\mu gC\ g^{-1}\ h^{-1}$)	β(SQT) ($°C^{-1}$)	R^2 (SQT)
Deciduous										
Norway Maple	*Acer platanoides*	1	9	15 – 31	<0.01	n/a	n/a	0.02	0.20	0.91
Red Maple	*Acer rubrum*	2[c], 2	22[c], 18	13[c] – 40[c], 14 – 45	0.70 – 0.72[c,e], 1.28 – 1.57 (1.02)	0.17[e] – 0.26[c], 0.15	0.71[e] – 0.81[c], 0.79	0.03 –0.23[c], 0.01	0.15 – 0.16[c], 0.10	0.32 – 0.70[c], 0.93
Sugar Maple	*Acer saccharum*	1	6	20 – 32	<0.01	0.15	1.00	0.04	0.18	0.77
Silver maple	*Acer saccharinum*	1	8	14 – 41	2.22	0.20	0.98	<0.01	n/a	n/a
Paper birch	*Betula papyrifera*	I[c]	17[c]	22[c] – 38[c]	4.78[c,e]	0.14[c,e]	0.88[c,e]	0.03[c]	0.27[c]	0.57[c]
American Chestnut	*Castanea dentata*	1	5	12 – 19	<0.01	n/a	n/a	<0.01	n/a	n/a
Northern Catalpa	*Catalpa speciosa*	1	10	16 – 42	<0.01	n/a	n/a	<0.01	0.17	0.83
Eucalyptus	*Eucalyptus globulus*	3	14	10 – 34	0.06 (0.06) – 0.08 (0.05)	–	–	0.01 (0.01) – 1.20 (1.10)	–	–
Green Ash	*Fraxinus pennsylvanica*	1	9	12 – 27	0.07 (0.07)	–	–	<0.01	n/a	n/a
Tulip Poplar	*Liriodendron tulipifera*	2	29	19 – 41	0.80[e] – 1.36[e]	0.19[e]–0.25[e]	0.65[e]–0.68[e]	0.01	0.20	0.62
Crab Apple	*Malus ionesis*	2	17	13 – 38	<0.01	n/a	n/a	<0.01	n/a	n/a
Narrow Leaf Cottonwood	*Populus angustifolia J.*	3	32	5 – 36	0.15 (0.07) – 0.43	0.11 – 0.35	0.79 – 0.98	<0.01	n/a	n/a
Cottonless Cottonwood	*Populus deltoide*	2	28	12 – 30	<0.01 – 0.11	0.25	0.86	<0.01	n/a	n/a
Big-tooth Aspen	*Populus grandidentata*	3[c]	38[c]	12[c] – 42[c]	0.22 (0.10) – 0.56 (0.69)[c]	–	–	<0.05 – 0.08 (0.00l)[c]	n/a	n/a
Trembling Aspen	*Populus tremuloides*	1	7	22 – 44	0.08 (0.02)	–	–	<0.01	n/a	n/a
Fire Cherry	*Prunus pennsylvanica*	1	3	29 – 42	0.37 (0.36)	–	–	0.06 (0.06)	n/a	n/a
Cherry	*Prunus virginiana*	1	8	14 – 37	1.45	0.21	0.82	<0.01	n/a	n/a
Swamp White Oak	*Quercus bicolor*	1	21	7 – 32	<0.01	n/a	n/a	n/a	n/a	n/a
Burr Oak	*Quercus macrocarpa*	1	25	4 – 35	<0.01	n/a	n/a	n/a	n/a	n/a
Pin Oak	*Quercus palustris*	1	10	17 – 42	0.05	0.09	0.92	n/a	n/a	n/a
Red Oak	*Quercus rubra*	3[c]	36[c]	19[c] – 39[c]	0.12 – 3.00[c]	0.06 – 0.16[c,e]	0.18 – 0.76[c,e]	0.03 – 0.53[c]	0.03 – 0.17[c]	0.14 – 0.70[c]
Schumard Oak	*Quercus shumardii*	1	18	7 – 28	<0.01	n/a	n/a	n/a	n/a	n/a
Coniferous										
Balsam Fir	*Abies balsamea*	1	5	21 – 40	3.40 (2.60)	–	–	0.01 (0.01)	–	–
Grand Fir	*Abies grandis*	1	15	10 – 33	0.36 (0.27)	–	–	<0.01	n/a	n/a
Blue Spruce	*Picea pungens*	3	40	1 – 47	0.13 – 0.70	0.10 – 0.14	0.81 – 0.91	<0.01 – 0.13	0.06 – 0.12	0.85 – 0.87
Shortleaf Pine	*Pinus echinata*	1	10	11 – 24	0.44 (0.38)	–	–	0.09	0.07	0.09
Ponderosa Pine	*Pinus ponderosa*	2	16	11 – 43	0.27 – 0.73	0.10 – 0.12	0.81 – 0.84	0.02 – 0.11	0.15 – 0.16	0.88 – 0.96
Red Pine	*Pinus resinosa*	3	37	15 – 40	0.05 – 0.99 (0.22)	0.08 – 0.10	0.36 – 0.49	0.03 – 0.14 (0.02)	0.21 – 0.26	0.68 – 0.79
Gray "Digger" Pine	*Pinus sabiniana*	1	7	23 – 33	4.02	0.21	0.59	0.06	0.29	0.94
White Pine	*Pinus strobus*	4[c], 3	47[c], 29	13[c] – 43[c], 15 – 45	0.18 (0.15) – 1.35[c], 0.18 (0.07) – 1.11 (0.76)	–	–	<0.01 – 035[c], 0.02 – 0.09	0.05[c], 0.08 – 0.11	0.04[c], 0.79 – 0.97
Scots pine	*Pinus sylvestris L.*	1	10	19 – 31	1.70	0.28	0.91	<0.01	n/a	n/a
Loblolly pine	*Pinus teada*	7[d], 3	144[d], 20	7[d] – 40[d], 18 – 38	0.06 – 0.62[d], 0.79 – 0.97	0.07 – 0.12[d], 0.08 – 0.13	0.34 – 0.73[d], 0.81 – 0.96	0.07 – 0.62[d], 0.03 – 0.04	0.14 – 0.21[d], 0.15 – 0.22	0.57 – 0.90[d], 0.90 – 0.98
Douglas Fir	*Pseudotsuga menziesii*	2	18	11 – 29	0.22 (0.06) – 3.40	0.24	0.73	<0.01 – 0.10 (0.06)	n/a	n/a
Redwood	*Sequoia sempervirens*	2	17	11 – 42	0.61 (0.10) – 2.76	0.06	0.82	0.09 – 0.10	0.14	0.84 – 0.96
Western Red Cedar	*Thuja plicata*	1	10	9 – 35	0.30 (0.18)	–	–	<0.01	0.13	0.88

Crops									
Fennel	*Ferula communis*	1	2	16 – 50	5.60 (2.50)	–	–	<0.01	n/a	n/a
Sunflower	*Helianthus*	6	38	15 – 36	0.41 (0.03) – 0.66	0.15	0.85	0.09 – 1.15	0.10 – 0.48	0.83 – 0.96
Rose of Sharon	*Hibiscus syriacus*	1	10	17 - 38	<0.01	n/a	n/a	<0.01	n/a	n/a
Tomato	*Lycopersicon*	1	10	16 – 34	0.17	0.19	0.79	<0.01	n/a	n/a
Bean Plant	*Phaleolus*	2	20	15 – 31	<0.01	n/a	n/a	<0.01	n/a	n/a
Tobacco	*Nicotiana*	4	32	14 – 29	<0.01	n/a	n/a	<0.01	n/a	n/a
Corn	*Zea mays var.*	4	33	15 – 33	<0.01 – 0.05	0.12 – 0.17	0.81 – 0.98	0.07 (0.03) – 0.19	0.18	0.84 – 0.98
Wheat	*Triticum*	2	20	14 – 29	<0.01	n/a	n/a	<0.01	n/a	n/a
Shrubs										
Shining Sumac	*Rhus glabra*	1	5	11 – 32	4.17 (1.91)	n/a	n/a	0.44 (0.10)	n/a	n/a
Juniper Bush	*Juniperus*	1	10	18 – 34	0.04	0.15	0.78	<0.01	0.18	0.90

Values separated by a hyphen indicte a range of values obtained from multiple enclosures as listed in column 3.

[a] For basal emission rates of the form x.xx (x.xx), the ERs were not fitted to an exponential curve, rather they are reported as the mean (with standard deviation in parenthesis) after normalizing each sample to 30 °C using a β of 0.10 °C^{-1} for MT.

[b] For basal emission rates of the form x.xx (x.xx), the ERs were not fitted to an exponential curve, rather they are reported as the mean (with standard deviation in parenthesis) after normalizing each sample to 30 °C using a β of 0.17 °C^{-1} for SQT.

[c] Individual sample data was reported in Ortega et al. (2007), summary results are included here for comparison of emissions with other species.

[d] Individual sample data was reported in Helmig et al. (2006), summary results are included here for comparison of emissions with other spoecies.

[e] MT ER are light dependent and ERs were corrected for light prior to fitting exponentially using Cpar (=2.878*0.001*PAR/((1 + 0.0027^2*PAR^2)$^{0.5}$)).

mentioned, the greatest MT emission rates from deciduous trees (up to ~5 μg C g^{-1} h^{-1}) were light dependent. Several of the non-conifer vegetation types were found to be "non-emitters" (i.e. had emission rates below the detection limits of the experiment). In addition to the high variability in emission rates between different tree species, there was also considerable emission rate variability (by up to a factor of 10) between individuals from the same species. For example, in seven individual loblolly pine enclosures, the MT emission rates ranged from 0.06 to 0.62 μg C g^{-1} h^{-1} and the SQT emission rates ranged from 0.07 to 0.62 μg C g^{-1} h^{-1}. Similarly, in three separate red oak enclosures, MT and SQT emission rates ranged from 0.1 to 3.0 μg C g^{-1} h^{-1}, and 0.03 to 0.53 μg C g^{-1} h^{-1}, respectively.

It is important to be aware of this high degree of variability in emission factors. As can be seen from Table 1, the absolute values of basal emission rates can be approximately the same as their variability, indicating that depending on the specimen tested, the emission rate could be substantial or negligible. Also, the emission factor variability among individuals from one species can be of the same order as the variability between species. Given this realization, one could make the argument that with a limited data set, there is no justification for claiming that emission rates from one species are statistically different than another similar species. In summary, noteworthy conclusions from the review of these data are:

- Entries in Table 1 represents a limited number of samples from a variety of vegetation species.
- Although limited in the number of replicates from any particular species, the data provide valuable insight into the variability and magnitude of emissions as well as their light and temperature dependencies.
- More systematic studies are required for individuals of the same species to provide better constraints on the control of emission rate and β-factor ranges.
- Analysis of a high number of individual measurements are recommended to allow for a rigorous statistical analysis in order to determine the number of samples required for statistically significant descriptions of quantitative emission behavior.

3.8. Monoterpene and sesquiterpene speciation

Tables 2A and 2B list the MT and SQT speciation for these experiments. The order of MT and SQT listed along the top row of these tables was determined by their elution order on a DB-1 GC column (which was used for the laboratory GC instrument). The most common MT observed from conifer species included α-pinene, camphene, β-pinene, β-myrcene, 3-carene, and *d*-limonene. Deciduous tree species generally emitted fewer individual MT species. The most common compounds observed were α-pinene, camphene, β-myrcene and both the *cis*- and *trans*-isomers of ocimene. For certain species, up to 100% of total MT emissions were from ocimene. Crops and shrubs showed similar MT speciation results to the deciduous tree species. The most common SQT observed from all vegetation types was β-caryophyllene. Other common SQT observed were bergamotene, humulene, muurolene, and both α and β farnesene. The MT and SQT speciation results are important as the molecular structure determines the chemical behavior in the atmosphere. Compounds with multiple double bonds and/or without ring structures are typically more reactive with respect to atmospheric oxidants, and their atmospheric lifetimes can be less than a few minutes. Therefore, when using BVOC emission rate data to model whole-canopy fluxes and their influences on atmospheric processes, the total emission rates, variability, light dependence, and speciation are all critical parameters to consider.

Table 2A
Speciation of monoterpene compounds in emission samples (% of each compound of the total monoterpene emissions)

Common Name	Genus / species	Total MT BER[a] (with stdev) (μgC g^{-1} hr^{-1})	cyclofenchone	bomene	tricyclene	α-thujene	α-pinene	camphene	sabinene	β-pinene	β-myrcene	α-phellandrene	3-carene	α-terpinene	o-cymene	p-cymene	β-terpinene	β-phellandrene	1,8-cineole	limonene	cis-ocimene	trans-ocimene	γ-terpinene	cis-linalool oxide	fenchone	trans-linalool oxide	para-cymenene	4-carene	terpinolene	β-linalool	α-thujone	β-thujone	allo-ocimene	cis-verbenol	camphor	camphene hydrate	borneol	4-terpineol	α-terpineol	dimethylnonatriene
Deciduous																																								
Norway Maple	*Acer platanoides*	<0.01																																						
Red Maple	*Acer rubrum*	1.28				6	10	1		37	20	2		8							1	1	6					3	2								1	2		
Red Maple	*Acer rubrum*	1.57 (1.02)				7	12	1		42	16	2		4	3						1	1	5					2	2								1	1		
Red Maple	*Acer rubrum*	0.70[b]					17	7		35	18									12		10	1																	
Red Maple	*Acer rubrum*	0.72[b,d]																			6	83																		11
Sugar Maple	*Acer saccharum*	0.01																				100																		
Silver maple	*Acer saccharinum*	2.22				11	2			33	9	2		9		5		6		4			12					3	1								1	1		
Paper birch	*Betula papyrifera*	4.78[b,d]				3	6	1		2	2	2		10				2		4	13	32	16						5		2								
American Chestnut	*Castanea dentata*	<0.01																																						
Northern Catalpa	*Catalpa speciosa*	<0.01																																						
Eucalyptus	*Eucalyptus globulus*	0.08 (0.05)					9		3		34		5						27		13	9																		
Eucalyptus	*Eucalyptus globulus*	0.06 (0.06)																			100																			
Eucalyptus	*Eucalyptus globulus*	0.31																			100																			
Green Ash	*Fraxinus pennsylvanica*	0.07 (0.07)																			67	33																		
Tulip Poplar	*Liriodendron tulipifera*	1.36[d]					1			1	2									11	4	76							1		3		1						1
Crab Apple	*Malus ionesis*	<0.01																																						
Crab Apple	*Malus ioensis*	<0.01																																						
Narrowleaf Cottonwood	*Populus angustifolia J.*	0.15 (0.07)					11	5		8										17	8	51																		
Narrowleaf Cottonwood	*Populus angustifolia J.*	0.43										5									7	9							79											
Narrowleaf Cottonwood	*Populus angustifolia J.*	0.36																				35							65											
Cottonless Cottonwood	*Populus deltoides*	<0.01																																						
Cottonless Cottonwood	*Populus deltoides*	0.11																				48							52											
Big-tooth Aspen	*Populus grandidentata*	0.56 (0.69)[b]					16	4		7	6							1		51		16																		
Big-tooth Aspen	*Populus grandidentata*	0.4[b,d]					21	80																																
Big-tooth Aspen	*Populus grandidentata*	0.22 (0.10)[b]					3	3			24									39		21																		
Trembling Aspen	*Populus tremuloides*	0.08 (0.02)					25		10	41										6		13							5											
Trembling Aspen	*Populus tremuloides*	<0.03																																						
Trembling Aspen	*Populus tremuloides*	1.30 (1.90)					13	5		21	11											50																		
Fire Cherry	*Prunus pennsylvanica*	0.37 (0.36)					66			34																														
Cherry	*Prunus virginiana*	1.45									1										3	96																		
Swamp White Oak	*Quercus bicolor*	<0.01																																						
Burr Oak	*Quercus macrocarpa*	<0.01																																						
Pin Oak	*Quercus palustris*	0.05							65													21	14																	
Red Oak	*Quercus rubra*	3.00[b]				6	9		14		10										4	53	5																	
Red Oak	*Quercus rubra*	0.12[b]			1		1	2													5	73							2		5								2
Red Oak	*Quercus rubra*	2.03[b,d]																			6	92																		2
Schumard Oak	*Quercus shumardii*	<0.01																																						
Cascara Buckthorn	*Rhamnus purshiana*	<0.01																																						

Table 2A *(continued)*

Crops																																							
Fennel	*Ferula communis*	5.60 (2.50)					13		2		5		48		10			4		5			1		11														
Sunflower	*Helianthus annuus*	0.66				1	24	2	20		4	1			2			3		29	2	11	2																
Sunflower	*Helianthus annuus*	0.43 (0.09)					26	3		26	4	3		3			3			17		9	5					1											
Sunflower	*Helianthus annuus*	0.56 (0.10)					46	3		17	3	1		2			3			9	2	10	3					1											
Sunflower	*Helianthus annuus*	0.41 (0.03)					50	3		18				1			2			11	2	10	2					1											
Sunflower	*Helianthus annuus*	0.44 (0.31)					18		21						5					34		18						4											
Rose of Sharon	*Hibiscus syriacus*	<0.01																																					
Tomato	*Lycopersicon esculetum*	0.17																56		44																			
Kidney Bean (x2)	*Phaseolus vulgaris*	<0.01																																					
Tobacco (x4)	*Nicotiana tabacum*	<0.01																																					
Corn	*Zea mays var. rugosa*	<0.01																																					
Corn	*Zea mays var. rugosa*	0.04																											100										
Corn	*Zea mays var. rugosa*	0.05																											100										
Corn	*Zea mays var. rugosa*	0.03																											100										
Wheat (x2)	*Triticum*	<0.01																																					
Coniferous																																							
Balsam Fir	*Abies balsamea*	3.40 (2.60)					18	15		56	5							6																					
Grand Fir	*Abies grandis*	0.36 (0.27)					7	14	14		26		3		1			35																					
Blue Spruce	*Picea pungens*	0.13					4	25		8		2	3		31					37			5						14						13				
Blue Spruce	*Picea pungens*	0.64					13	11		4	15		3							46															7		1		
Blue Spruce	*Picea pungens*	0.70					7	4		2	22		1						3	26		2							1	13					12	3	2		2
Shortleaf Pine	*Pinus echinata*	0.44 (0.38)				1	5		27		23		20		1			1		10			1						10										
Ponderosa Pine	*Pinus ponderosa*	0.27					19	1	15		15		13							8	1	1	1	1		1				11									12
Ponderosa Pine	*Pinus ponderosa*	0.73				1	10		4		26				1				17	10		1	1	2		4			1	5								1	17
Red Pine	*Pinus resinosa*	0.80	1	1	5		16	26		3	14	1	5	1		4				10			3				1			3					1		4		
Red Pine	*Pinus resinosa*	0.99 (0.22)					42	3		29	20		5						2																				
Red Pine	*Pinus resinosa*	0.05			3		39	13		16	11		3	1		2				12																			
Gray "Digger" Pine	*Pinus sabiniana*	4.02					44				13									34		9																	
White Pine	*Pinus strobus*	0.19					33	6		14	9	2			2			7		8			1			1			1						5	3	6	1	2
White Pine	*Pinus strobus*	0.91					25	4		28	10	2			1			11		10				1		1			2	1					1		2		1
White Pine	*Pinus strobus*	0.97					25	8		16	28								5	2						2		1		1					6		5		1
White Pine	*Pinus strobus*	0.18 (0.15)[b]					44	8		24	13							5		5																			
White Pine	*Pinus strobus*	1.35[b]	1	1	2		21	17		8	5	2		1		1			27	4			1							9									
White Pine	*Pinus strobus*	1.00[b]					31	5		42	11							7		4																			
White Pine	*Pinus strobus*	0.36[b]	1	2	4		21	23	4	7		4		2		6		1		15	1		1							6									
Beach Pine	*Pinus sylvestris*	0.17				1	6		26		5		15		1			1		30			2						13										
Scots Pine	*Pinus sylvestris L.*	1.7					13	6	18		13		17						23	10																			
Loblolly Pine	*Pinus teada*	0.06[c]					61	14		1		4		2		1		1					2				11								3				
Loblolly Pine	*Pinus teada*	0.21[c]					74	10		3		3		1		1		1					2				4								1				
Loblolly Pine	*Pinus teada*	0.23[c]					73			5	5									17																			
Loblolly Pine	*Pinus teada*	0.166					38			16	44																												2
Loblolly Pine	*Pinus teada*	0.10					38			17	26																			18									1
Loblolly Pine	*Pinus teada*	0.06					38			19	15							28																					
Douglas Fir	*Pseudotsuga menziesii*	3.40			3		11	29		7	7		8							31									1										
Douglas Fir	*Pseudotsuga menziesii*	0.22 (0.06)					22	14		33																									32				
Redwood	*Sequoia sempervirens*	0.61 (0.10)				4	45	2	10	8		1			8			10					7						2									1	3
Redwood	*Sequoia sempervirens*	2.76				1	31		14		9	1			5			11		17		1	7						2	1									
Western Red Cedar	*Thuja plicata*	0.30 (0.18)				1	10		12	4			8										1						3		48	13							
Shrubs																																							
Sumac	*Rhus glabra*	4.17 (1.91)					15	2	17		7									2	3	53																	
Juniper Bush	*Juniperus sp.*	0.04				1	8	2	9		24									13	1	1	1	1					2	38									

[a] Basal MT emission rates of the form x.xx (y.yy) were not fitted to an exponential curve, rather they are reported as the mean (with standard deviation in parenthesis) after normalizing each measurement result to 30°C using a β of 0.10 °C^{-1}.

[b] Sample data was reported in Ortega et al., 2007. Summary results are provided here for comparison with other species.

[c] Sample data was reported in Helmig et al., 2006. Summary results are provided here for comparison with other species.

[d] Light-dependent MT. ERs were first corrected for standard light conditions (PAR=1000 mmol m^{-2} s^{-1}) using the correction factor Cpar (=2.878*0.001*PAR/((1+0.00272*PAR2)0.5)); The adjusted ERs were then plotted against temperature to determine β factors.

Table 2B
Speciation of sesquiterpene compounds in emission samples (% of each compound of the total sesquiterpene emissions)

Common Name	Genus / species	Total SQT BER[a] ($\mu gC\ g^{-1}\ hr^{-1}$)	δ-elemene	α-cubebene	α-copaene	β-bourbonene	β-cubebene	β-elemene	*iso*-longifolene	neoclovene	α-cedrene	β-caryophyllene	β-gurjunene	neryl acetone	α-*trans*-bergamotene	aromadendrene	α-humulene	β-farnesene	*allo*-aromadendrene	acoradiene	γ-muurolene	δ-germacrene	β-selinene	γ-curcumene	α-selinene	germacrene B	α-muurolene	α-farnesene	β-bisabolene	γ-cadinene	δ-cadinene	γ-elemene	cedrol	β-sesquiphellandrene	*trans*-nerolidol
Deciduous																																			
Norway Maple	*Acer platanoides*	0.02				8						44										16						31							
Red Maple	*Acer rubrum*	0.03		17	7	16	6					27																18		9					
Red Maple	*Acer rubrum*	0.01 (0.003)										44													36					20					
Red Maple	*Acer rubrum*	0.23[b]										69			1			1										29							
Red Maple	*Acer rubrum*	0.03[b]																					100												
Sugar Maple	*Acer saccharum*	0.04										41					3											56							
Silver maple	*Acer saccharinum*	<0.01																																	
Paper birch	*Betula papyrifera*	0.03[b]																										100							
American Chestnut	*Castanea dentata*	<0.01																																	
Northern Catalpa	*Catalpa speciosa*	0.00						27																				73							
Eucalyptus	*Eucalyptus globulus*	1.20 (1.10)		3	11	8		1				40					9	4				9				10				2	2				
Eucalyptus	*Eucalyptus globulus*	0.02 (0.02)										38													44						20				
Eucalyptus	*Eucalyptus globulus*	0.01 (0.01)										27													51						22				
Green Ash	*Fraxinus pennsylvanica*	<0.01																																	
Tulip Poplar	*Liriodendron tulipifera*	0.01										100																							
Crab Apple	*Malus ionesis*	<0.01																																	
Crab Apple	*Malus ioensis*	<0.01																																	
Narrowleaf Cottonwood	*Populus angustifolia J.*	n/a[d]																																	
Narrowleaf Cottonwood	*Populus angustifolia J.*	n/a[d]																																	
Narrowleaf Cottonwood	*Populus angustifolia J.*	n/a[d]																																	
Cottonless Cottonwood	*Populus deltoides*	n/a[d]																																	
Cottonless Cottonwood	*Populus deltoides*	n/a[d]																																	
Big-tooth Aspen	*Populus grandidentata*	0.08 (0.00)[b]										10																90							
Big-tooth Aspen	*Populus grandidentata*	<0.05[b]																																	
Big-tooth Aspen	*Populus grandidentata*	n/a[b,d]																																	
Trembling Aspen	*Populus tremuloides*	<0.01																																	
Trembling Aspen	*Populus tremuloides*	<0.01																																	
Trembling Aspen	*Populus tremuloides*	0.92 (0.64)																										100							
Fire Cherry	*Prunus pennsylvanica*	0.06 (0.06)																62										38							
Cherry	*Prunus virginiana*	<0.01																																	
Swamp White Oak	*Quercus bicolor*	n/a[d]																																	
Burr Oak	*Quercus macrocarpa*	n/a[d]																																	
Pin Oak	*Quercus palustris*	0.02									40	60																							
Red Oak	*Quercus rubra*	0.43[b]			6	20						33	5				2		8			12				2		12							
Red Oak	*Quercus rubra*	0.53[b]				23		24				15																38							
Red Oak	*Quercus rubra*	0.03b																										100							
Schumard Oak	*Quercus shumardii*	n/a[d]																																	
Cascara Buckthorn	*Rhamnus purshiana*	<0.01																																	

Table 2B (*continued*)

Crops																																		
Fennel	*Ferula communis*	<0.01																																
Sunflower	*Helianthus annuus*	0.09					11				29			6		5	3					47												
Sunflower	*Helianthus annuus*	1.15	2	3		1	2				55	2		8		4	5			6			5			1			2	3			1	
Sunflower	*Helianthus annuus*	0.99	2	3		2	5				62	2		11		3	5													3			2	
Sunflower	*Helianthus annuus*	0.23 (0.06)		4		2	7				54	2		18		3	10																	
Sunflower	*Helianthus annuus*	0.59	1	2				3	2	5	68	1		1	1	9														7				
Rose of Sharon	*Hibiscus syriacus*	<0.01																																
Tomato	*Lycopersicon esculetum*	<0.01																																
Kidney Bean (x2)	*Phaseolus vulgaris*	<0.01																																
Tobacco (x4)	*Nicotiana tabacum*	<0.01																																
Corn	*Zea mays var. rugosa*	0.15																								44							56
Corn	*Zea mays var. rugosa*	0.12 (0.04)																								50							50
Corn	*Zea mays var. rugosa*	0.19																								32							68
Corn	*Zea mays var. rugosa*	0.07 (0.03)																								41							59
Wheat (x2)	*Triticum*	<0.01																																
Coniferous																																		
Balsam Fir	*Abies balsamea*	0.01 (0.01)															53										47							
Grand Fir	*Abies grandis*	<0.01																																
Blue Spruce	*Picea pungens*	<0.01																																
Blue Spruce	*Picea pungens*	0.12															25										75							
Blue Spruce	*Picea pungens*	0.13															58										42							
Shortleaf Pine	*Pinus echinata*	0.09												100																				
Ponderosa Pine	*Pinus ponderosa*	0.02	5	1	2						28					15	10			11	10								8	8				
Ponderosa Pine	*Pinus ponderosa*	0.11	3	2							16					5	43			9	10								6	5				
Red Pine	*Pinus resinosa*	0.075				11											52					9						26	2					
Red Pine	*Pinus resinosa*	0.14 (0.02)															64										36							
Red Pine	*Pinus resinosa*	0.03				2											6											92						
Gray "Digger" Pine	*Pinus sabiniana*	0.06															77										20							
White Pine	*Pinus strobus*	0.09			5						11				3	13		2		32	13					1	9		8	3				
White Pine	*Pinus strobus*	0.09	1	2	2	1					20	2			2	7		2		15	9			3		3	2		14	14				
White Pine	*Pinus strobus*	0.02									25					34	3										30			8				
White Pine	*Pinus strobus*	0.03 (0.04)[b]																									100							
White Pine	*Pinus strobus*	0.35[b]				13				4						15						25				38				6				
White Pine	*Pinus strobus*	0.02[b]									22						8										70							
White Pine	*Pinus strobus*	<0.01[b]																																
Beach Pine	*Pinus sylvestris*	0.10									6			77			3				5					1	4			5				
Scots Pine	*Pinus sylvestris L.*	<0.01																																
Loblolly Pine	*Pinus teada*	0.07[c]									22			3		8	5			62														
Loblolly Pine	*Pinus teada*	0.12[c]									35			10		9	29			17														
Loblolly Pine	*Pinus teada*	0.26[c]					4			3	22		2	15		5	18			2	2						4	5		3	14	2		
Loblolly Pine	*Pinus teada*	0.03	1	1			2			1	38	3		3	1	16				5	5			2		5			7	9				
Loblolly Pine	*Pinus teada*	0.04	8	1			1			1	52	1		5		21				2	1			1		4			4	8				
Loblolly Pine	*Pinus teada*	0.04								2	54			2		30										5				7				
Douglas Fir	*Pseudotsuga menziesii*	<0.01																																
Douglas Fir	*Pseudotsuga menziesii*	0.10 (0.06)																	43								57							
Redwood	*Sequoia sempervirens*	0.10														45	7										41				7			
Redwood	*Sequoia sempervirens*	0.09	9	3			8				13					10	1				9					4			2	5	26			
Western Red Cedar	*Thuja plicata*	<0.01					27												73															
Shrubs																																		
Sumac	*Rhus glabra*	0.44 (0.10)									50					30	20																	
Juniper Bush	*Juniperus sp.*	<0.01	8								15																		60	16				

[a] Basal SQT emission rates of the form x.xx (y.yy) were not fitted to an exponential curve, rather they are reported as the mean (with standard deviation in parenthesis) after normalizing each measurement result to 30°C using a β of 0.17 °C^{-1}.

[b] Sample data was reported in Ortega et al., 2007. Summary results are provided here for comparison with other species.

[c] Sample data was reported in Helmig et al., 2006. Summary results are provided here for comparison with other species.

[d] Sesquiterpenes could not be identified because of instrumental difficulties. Vegetation species are included for consistency with Table 2A.

4. Conclusions

BVOC emission studies from vegetation enclosures can address scientific questions in a variety of fields ranging from atmospheric chemistry to ecology. Branch enclosure experiments can be especially useful for studying low-volatility, highly reactive, and aerosol-forming compounds such as oxygenated BVOC, certain MT and SQT for which routine analytical techniques for above-canopy flux measurements are not yet available. Enclosure techniques are currently the preferred method for estimating whole-canopy fluxes of these compounds. In situ, analytical methods for monitoring emission rates in enclosures have a number of advantages over techniques where sample collection in the field with subsequent laboratory analysis is required. These advantages include a higher sampling frequency, lower potential for analytical artifacts, and the ability to easily adjust experimental protocols in the field in response to readily available data. Addition of a chemical reference standard to the enclosure purge air has proven invaluable for identifying compound recovery rates. These results also suggest the necessity for correcting determined emission rates for potential adsorption losses of BVOC compounds in the enclosure system.

Previous studies published in the literature demonstrate highly variable procedures and analytical techniques. We have emphasized critical experimental details in order to minimize vegetation disturbances, and reduce analytical losses (from adsorption and reactions with oxidants), in an effort to improve data accuracy. Carefully executed experiments have demonstrated a wide range of emission rates from multiple vegetation species at a variety of field sites. A number of tree species were shown to exhibit light-dependent MT emissions. There are currently inadequate explanations that describe how factors other than light and temperature can influence BVOC emissions. Consequently, atmospheric models cannot incorporate this variability in emission factors that is observed in enclosure experiments. More systematic studies are recommended to provide a better quantitative understanding of these processes.

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Appendix A. Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.chemosphere.2008.02.054.

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