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Sesquiterpenoid Emissions from Agricultural Crops: Correlations to Monoterpenoid Emissions and Leaf Terpene Content

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Emissions of biogenic volatile organic compounds (BVOCs) are important precursors to both ozone and secondary organic aerosol formation. In this study, we identify and quantify volatile (C_{10}) and intermediate-volatility (C_{15}) BVOCs stored in and emitted from 22 prominent woody and herbaceous crops with a particular focus on sesquiterpenoids (SQTs), which have presented measurement challenges in previous studies. Monoterpenoids (MNTs) and SQTs were simultaneously emitted from all the crops studied; there were significant correlations between emission rates and leaf content for both MNTs and SQTs and additional correlations between MNTs and SQTs in both emissions and leaf content. Our results suggest that species with high concentrations of stored terpenoids in their leaves, such as those grown commercially for their essential oil content, are likely high BVOC emitters. Emissions from agricultural species were dominated by SQTs at low MNT emission rates (on the order of several tens of ng/(g_{DM}·h)), while at higher MNT levels (on the order of several hundreds of ng/(g_{DM}·h)), SQT emissions were approximately equivalent. Based on our empirical correlations, we estimate that global SQT emissions are similar to MNT emissions and on the order of 100 Tg yr^{-1}, which justifies the need for better representation of SQTs in both BVOC emission and atmospheric models.

Introduction

Agricultural regions of California, such as the San Joaquin Valley, frequently see high concentrations of both tropospheric ozone (O_3) and secondary organic aerosol (SOA) due to elevated emissions of biogenic and anthropogenic precursors, and increased photochemical processing that accompany high ambient temperatures; all counties in the San Joaquin Valley are out of compliance with California and U.S. Environmental Protection Agency air quality standards, for 1-h O_3, 8-h O_3, and particulate matter (PM-2.5) (*1*) (http://www.arb.ca.gov/enf/complaints/complaints.htm). The study of these pollutants and their precursors is crucial since both O_3 and PM have detrimental impacts on human health and can influence climate change. Biogenic volatile organic compounds (BVOCs) are key precursors of O_3 and SOA, which contribute to PM loading. VOCs (of either biogenic or anthropogenic origin), when combined with anthropogenic nitrogen oxides in the presence of UV radiation, lead to the formation of O_3. The reaction of VOCs with atmospheric oxidants (e.g., hydroxyl radicals, ozone, and nitrogen oxides) also leads to the formation of SOA. In addition to the health effects associated with O_3, it causes a positive radiative forcing—both directly as a greenhouse gas and indirectly by causing physiological plant damage and thus reducing carbon storage potential and plant productivity (*2, 3*). SOA also causes an important but highly uncertain forcing of climate since refractive aerosols increase planetary albedo; the associated light scattering leads to increased levels of diffuse sunlight, which has significant yet disputed effects on carbon uptake by plants (*4, 5*). BVOC emissions in regions with substantial tropospheric air pollution have been shown to form enough SOA to cause regional cooling (*6*).

Terpenoids (i.e., oxygenated and nonoxygenated terpenes) are the largest and most diverse class of BVOCs. Unlike hemiterpenoids (e.g., isoprene and methyl-butenol), monoterpenoids (MNTs), sesquiterpenoids (SQTs), and other nonterpenoid compounds accumulate in high concentrations within a variety of specialized plant storage structures, such as secretory cells, secretory cavities, ducts, glandular trichomes, and glands. BVOCs are either supplied to glands by vascular tissues or synthesized by their constituent cells, and their purposes include mediating interactions between the plant and other organisms and providing response mechanisms to cope with biotic and abiotic stresses (*7*).

Concentration of BVOCs in specialized secretory structures affects the diffusion of volatiles from cells into intercellular spaces and the atmosphere (*8, 9*). Diffusion occurs along vapor-pressure gradients from relatively high concentrations in cellular compartments to the air surrounding the leaf, where lower concentrations persist due to atmospheric dilution and chemical processing. Cellular secretion and subsequent emission of volatile substances are generally associated with these storage structures, but previous work has focused on either storage or emission of BVOCs from leaves, and little work has been done to determine their relationship. In comparison with other terpenoids, few studies have effectively measured and reported SQT emissions, for either crop or natural species. This is largely due to difficulties in measuring SQTs since significant fractions are lost in sampling systems via condensation and chemical reactions, owing to low volatilities and short atmospheric lifetimes (*10*). As a result, estimations of SQT emissions from vegetation in the published literature are highly uncertain.

The objectives of this study were to measure leaf emissions and leaf storage of BVOCs for some of the most representative crop species in California, with chemical speciation of C_{10}-C_{15} compounds; evaluate correlations between BVOC emission rates and storage within foliage and the relationship between different biochemical classes of BVOCs; and explore

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whether SQT emissions could be estimated based on those empirical correlations. While we did focus on California crops, the results are widely applicable since these crops are cultivated in many areas.

Materials and Methods

Greenhouse Measurement Setup. We used a greenhouse facility in Berkeley, California, to house 5−10 plants for each of the 22 potted species studied. Detailed information about the species, their cultivar, the number of plants sampled, and their secretory structure type is shown in Table S1.

For each crop species, 3 to 6 plants were randomly sampled from July 25th to October 22nd 2008 after they had adapted to greenhouse conditions for at least 5 months. Plants were watered daily and fertilized weekly to ensure favorable growing conditions. Daytime temperatures in the greenhouse ranged between 25−30 °C and a glass roof on the greenhouse allowed ambient lighting, including photosynthetically active radiation (PAR), to reach the plants. Relative humidity was maintained in the range of 40−60%.

Sampling Device. Two dynamic branch enclosures were designed to simultaneously sample BVOC emissions from two plants. Either a branch (woody species) or the entire plant (herbaceous species) was enclosed in a 80 L cylindrical enclosure constructed out of Teflon. Air supplied to the enclosures was purified of O_3, CO_2, and hydrocarbons using a zero air generator (Aadco mod.737), and CO_2 was maintained at a constant concentration (380 ppm) by diluting pure CO_2 from a cylinder using a mass-flow controller (MKS Instruments, Inc.). Air flow into the enclosures was maintained at 10 L/min using a mass-flow controller and dispersed using a large diameter ring of Teflon tubing with multiple small holes to facilitate internal mixing.

Each enclosure was equipped with a radiation sensor (LICOR quantum sensor, Model Li-190), a relative humidity and temperature sensor (Omega Engineering, Model HX93 AV-RP1), and a system of wire thermocouples wrapped around branches and touching leaves to measure their temperatures (Omega Engineering, precision fine wire thermocouples).

Measurements of photosynthetic parameters (CO_2, H_2O, data not shown) and BVOC were carried out by switching between the two enclosure outflows every 15 min with a system of 2 and 3 way solenoid valves (TEQCOM Industries), controlled by a datalogger (Campbell Scientifics, model CR10). The first 3 minutes of each cycle were dedicated to the measurement of the zero air entering the enclosures. After sampling BVOC emissions, enclosed leaves were lyophilized and weighed in order to express BVOC emission rates on a dry mass (DM) basis. CO_2 and H_2O were measured by an infrared gas analyzer (Li-Cor 6262).

BVOC Emissions: Collection and Extraction. Measurements of BVOC emissions began ∼24 h after the plant was placed in the sampling system so that the plant could adjust to the enclosure. BVOCs emissions were trapped onto 50 mg of Super-Q adsorbent (Alltech, Columbia MD, USA) in a 6.3 mm diameter × 6 mm length glass tube placed just at the chamber outlet. The plant enclosures were sampled over two consecutive periods of 30−60 min each at a rate of 1 L/min. Preliminary laboratory tests checked for BVOC breakthrough using two glass tubes placed in series. Immediately after sampling, collection tubes were stored in a freezer prior to extraction.

Compounds trapped on the adsorbent were extracted following a slightly modified method from that described in ref *11*. Analytes were extracted using dichloromethane, which was collected in amber glass vials up to 1 mL. After extraction, the samples were concentrated by a factor of ∼10 in the laboratory by evaporating the solvent with a gentle nitrogen flow (∼100 mL/min) for ∼10 h and adjusting all the samples to the same final volume (100 uL) by adding hexane. For every set of samples that were concentrated, a solution containing known amounts of pure standards was also concentrated and used to account for analyte losses during the concentration process. A loss factor of 35 ± 8% was used when calculating the BVOC mass emitted, based on the analysis of these standards. Fluxes were calculated by multiplying the mass of BVOC emitted by the zero air flow entering the cuvette and dividing by the product of the sampling flow, sampling time, and dry mass of plant enclosed.

Basal emission rates (BER) were calculated at environmental conditions of $T = 30$ °C and PAR = 1000 μmol/(m^2·s) or at $T = 30$ °C according to the algorithms proposed by Guenther et al. (*12*). While light ultimately drives the synthesis of any carbon-based compound in BVOC storing species, emissions occur when BVOCs volatilize from the storing structures, and emission rates increase exponentially with temperature (*13, 14*). Unless specified differently, reported emissions in this study are BER standardized for temperature only; temperature and light-standardized results can be found in the Supporting Information.

BVOC Content: Extraction. After leaf emissions were sampled, the branch was removed from the enclosure, and the leaves of each plant were harvested and pooled together to extract their BVOC content. Prior to BVOC extraction, leaves were lyophilized in order to express results on a leaf DM basis. Terpene extraction by means of an organic solvent was then performed according to the method described in ref *15*.

Analyses of BVOC Emissions and Content. All samples were analyzed for BVOCs using a Varian CP-3800 gas chromatograph with a Saturn 2200 ion trap mass spectrometer. Ultrahigh purity helium was used as the carrier gas (1.0 mL/min) in a 30 m Rtx-5 capillary column (Varian, Palo Alto, CA, USA). The oven temperature was held at 43 °C for 8 min, ramped to 160 at 4 °C/min, to 260 at 7 °C/min, and to 300° at 20 °C/min, and then held for 5 min. The mass spectrometer was operated in mass scan mode from m/z 40 to 650. Analyte quantification was achieved through calibration using liquid-phase standards. Compound identification was based on the retention time of the injected pure standards and by comparing the mass spectrum of each compound to mass spectra from The National Institute of Standards and Technology (NIST) and Adams libraries (*16*). When pure standards were not available (Table S2, Supporting Information), tentative identification was achieved by comparing their mass spectrum to that shown in libraries, and quantification was based upon the calibration curve of a compound of the same chemical family. The identities of all compounds were also confirmed by checking their experimental arithmetic index (AI) against known values (*16*) (Table S2, Supporting Information).

Statistical Analyses. Statistical differences in BVOC content and emissions between herbaceous and woody plants were tested using the student t test. Linear and nonlinear regression analyses were used to determine correlations between emitted and stored compounds and between BVOCs of different biosynthetic classes. Regressions were compared for herbaceous and woody species in terms of slope and intercept using the ANOVA F test. All statistical analyses were done using Statgraphics centurion. Throughout the text, all uncertainties are expressed as standard errors.

Results and Discussion

Terpenoid and Nonterpenoid Emissions from Crops. Thirty-seven SQTs and 28 MNTs were identified in the emissions from the 22 crop species (Table S2, Supporting Information). For sesquiterpenes, the most diverse class of terpenoids in plants, fewer than 30 species had been identified so far as emitted from vegetation (*17, 18*). We also identified emissions

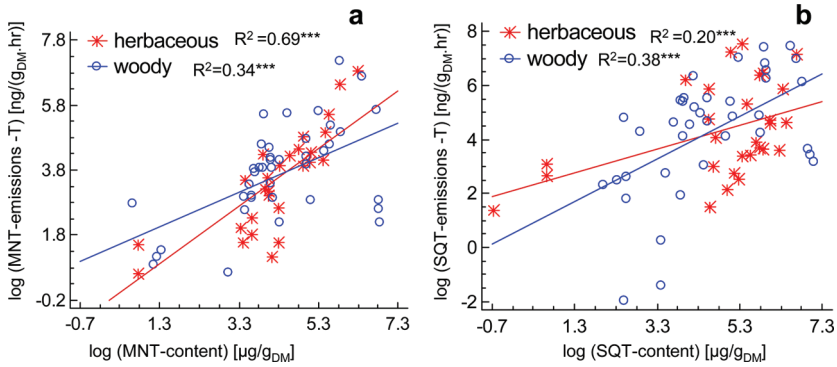

FIGURE 1. Relationship between stored and emitted monoterpenoids (MNTs, a) and sesquiterpenoids (SQTs, b) for herbaceous and woody plants. Each value represents a different plant (n = 73). Emissions are temperature-standardized at 30 °C. ***: $P < 0.001$. P: two-tailed significance level. A single R^2 is shown when significant difference in the regression lines occurred (see text).

of 7 benzenoids (BZ), 5 fatty acid derivates (FAD), and 1 nitrogen-containing compound (N).

With the exception of FAD content, which was higher in woody than in herbaceous species ($t = -2.52$, $P < 0.05$), no significant differences were observed between the emission rate or the storage of herbaceous and woody species (Table S3, Supporting Information). This was observed even though fast-growing species (e.g., herbaceous species) are expected to invest most of their energy in growth rather than in carbon-based defense compounds such as BVOCs (*19*).

For a few species, nonterpenoid compounds represented the major fraction of compounds emitted. Peach trees and table grape vines mainly released BZ emissions, while FADs dominated emissions of both apricot and carrot ("Red Navel"). Methyl salicylate (MeSA), the most prevalent BZ, was measured in the emissions of 9 crops. It has been suggested to be an important component of other agricultural and natural species (e.g., walnut, holm oak, Norway spruce) and to contribute to the missing VOC budget (*20–22*). 3-trans-Hexenyl acetate, an important FAD, was measured in the emissions from 5 crops, but, along with MeSA, it was not observed in leaf content. This result is reasonable because these compounds are associated with induced plant defense mechanisms and thus are not expected to be stored in specific storage structures in plant tissues (*23, 24*).

With the exception of the 4 major nonterpenoid emitters listed above, terpenoid emissions (i.e., MNTs and SQTs) were the dominant contributor to total emissions from crops. Limonene and β-caryophyllene, considered the most common MNTs and SQTs emitted from vegetation (*25–27*), were stored and released by all species. α-Pinene, β-pinene, and the SQTs α-humulene and α-farnesene were also present in the leaf emissions and content of a considerable number of species. Detailed information on the speciated BVOC emissions and leaf content for the 22 crops can be found in Figures S1 and S2 and Table S2 (Supporting Information).

We observed significant SQT emissions that were greater than MNTs in all but 3 of the crops measured, whereas past studies described crop species as being predominantly MNT emitters (*28*). The highest SQT BER, detected in almond, tomato, mandarin, and orange, were on the order of 1 μg/(g_{DM}·h). Consistent with our work, Ciccioli et al. (*29*) reported that SQTs comprised 50−70% of all detected hydrocarbons emitted by *Citrus* species during summer, although only β-caryophyllene was observed in their study. Furthermore, SQT emissions were detected from 7 (out of 8) pine species by Helmig et al. (*30*), suggesting that SQT emissions are almost always present for MNT-emitting species. Recent work on coniferous species supports this claim; they were considered to be nonemitters of SQTs in some past inventories (*31*), but recent research reports that SQT emissions account for a considerable fraction of total BVOC emissions during summer months (*32, 33*).

In some previous work, the relatively low volatilities and high reactivities of SQTs has likely caused underestimates and large uncertainties in emissions due to both physical and chemical losses in measurement systems. The studies of Ortega et al. (*26, 34*) and Helmig et al. (*35, 36*) compile a number of recommendations that should be adopted when attempting to measure SQT emissions from plants. For example, primary emissions of highly reactive compounds are better measured using branch enclosures, as they allow for the control of oxidant levels which would destroy highly reactive BVOC emissions while the branch remains as close to natural conditions as possible. Additionally, SQT emissions may undergo transformations during the collection process and adhere to materials commonly used in BVOC collection (i.e., tubing, trapping material, filters, etc.). As a result, the use of adsorbent filled cartridges directly connected to the branch enclosure is preferable to study SQT emissions.

Correlations between Terpenoid Emissions and Content. Total MNT BER were significantly correlated to total MNT content (Figure 1a, log−log plot). The slope was significantly higher for herbaceous species than for woody species (0.88 ± 0.12 vs 0.53 ± 0.10, respectively, $F = 4.59$, $P < 0.05$), indicating that for the same leaf MNT content, greater MNT emissions are expected for herbaceous species. SQT emissions were also correlated to SQT content with no statistical differences between woody and herbaceous species in either slope (0.78 ± 0.16 and 0.44 ± 0.17, respectively, $F = 1.74$, $P > 0.05$) or intercept (0.68 ± 0.78 and 2.2 ± 0.89, respectively, $F = 1.30$, $P > 0.05$) (Figure 1b). Comparing SQT emissions versus SQT leaf content for woody and herbaceous species yields a slope of 0.64 ± 0.12, an intercept of 1.1 ± 0.59 and a $R^2 = 0.33$ ($P < 0.001$).

We examined the possibility that changes in vapor pressure deficit (VPD) might have driven terpenoid emissions. Geron et al. (*37*) observed that elevating the VPD in the plant enclosure, by removing moisture from the incoming air, increased isoprene emissions of *Baccaurea ramiflora* Lour. from 0 to 10 μg/(g_{DM}·h). However, Nuñez et al. (*38*) reported that large VPDs (e.g., ~7 kPa) still lead to low BVOC emission rates. Since VPD values ranged from 0.77 to 4.03 KPa during our study, we considered the possibility that VPD-induced emissions could occur. We performed general linear model tests checking VPD and plant emissions for covariance with species as a factor; we found no significant effect of VPD on emission variability between species. We therefore exclude the possibility of VPD driving changes in BVOC emissions during our study.

Similar to other studies, we observed discrepancies between emissions and leaf content for a few species (*15, 39, 40*). In this study, lemon and mandarin stored large amounts of SQTs and MNTs, while their emissions were comparatively small. Moreover, qualitative differences were evident for lemon, orange, and potato, for which we detected

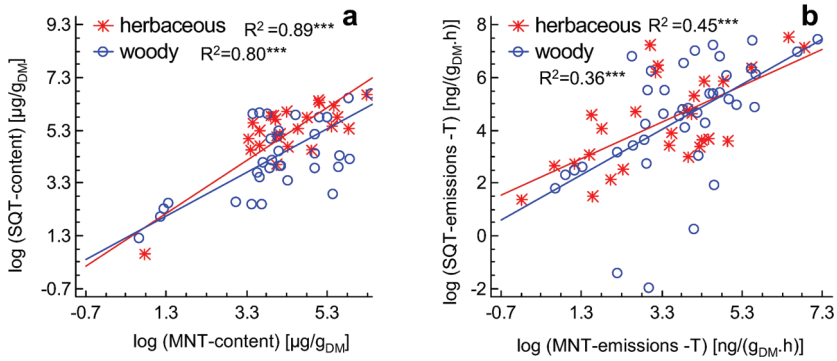

FIGURE 2. Relationship between monoterpenoids (MNTs) and sesquiterpenoids (SQTs) stored in leaves (a) or emitted by leaves (b) for herbaceous and woody plants. Each value represents a different plant (n = 73). Emissions are temperature-standardized at 30 °C. ***: P < 0.001. P: two-tailed significance level.

3 times the number of terpenoid compounds in their content compared to their leaf emissions (Figures S1 and S2 of the Supporting Information).

The low vapor pressure of SQTs is typically cited as the reason why SQT release to the atmosphere is less than that for MNTs at a given temperature. Additionally, internal resistances lead to insufficient passive diffusion and prevent the release of BVOC. In potatoes, the resistance to VOC diffusion is likely a function of the thickness of the glandular trichome wall. In some species of the mint family, which contain glandular trichomes, BVOCs have been observed to remain in certain reservoirs until the cuticle is burst by abrasion. When these resistances occur, an important fraction of leaf emissions originate from *de novo* synthesis, which takes place in mesophyll cells (*41, 42*). For discrepancies in *Citrus* species, the resistances limiting BVOC emission have more than one potential explanation. The resistance between secretory cavities and the atmosphere must be higher since BVOCs have to diffuse over the leaf membrane and the cell layers surrounding the cavity, a phenomenon that can be highly restricted if the outer peripheral cells have very thick walls. It can also be hypothesized that BVOC emission requires a transporter, such as lipid transfer proteins and ABC transporters (*43*). These transporters are believed to be involved in the secretion/emission of hydrophobic molecules from plant tissue. A limited amount of these transporters could explain why these molecules are retained within the tissue. Finally, differences between terpenoid emissions and content in peppermint leaves has been attributed to the existence of two types of foliage glands within the same species; one gland type would be the main source of terpenoid emissions, while the other would contain the bulk of the total leaf terpene content with other lypophilic compounds (*39*).

The relationship between leaf terpenoid emissions and content was first reported by Lerdau et al. (*44*) who showed a strong relationship between leaf MNT emissions and concentration within the leaf tissues of the Douglas fir (*Pseudotsuga menziesii* Mirb). Emissions of camphor (a MNT) and total SQTs from *Rosmarinus officinalis* L. showed similar correlations to their content in leaf tissue (*45*). Furthermore, similar relative quantities of SQTs were observed in leaf content and emissions from Copiaba (*Copaifera officinalis* Jacq. L.) (*46*). The results of our study and previous work support the classical assumption that differences in leaf terpenoid content lead to variations in terpenoid emissions and play a crucial role in the actual emission rates of stored compounds (*47*). Consequently, we suggest that species with high stored concentrations of terpenoids, typically species that are grown commercially for their essential oil content, could be identified as potential high BVOC emitters. This implies that the choice of crop or natural species containing low levels of stored BVOCs for massive scale cultivations or forest plantations would reduce their potential to adversely affect air quality. Additionally, low MNT and SQT concentrations in leaf litter decrease its flammability, reducing the risk of fire and associated air pollution (*48, 49*). It is worth noting that this finding does not preclude species without storage structures (e.g., *Quercus coccifera* L., *Quercus ilex* L.) from being high emitters. Nonetheless, the existence of a permanent reservoir of BVOCs within the range of several mg/g_{DM} accounts for a massive source of BVOC emissions during forest fires (*50*), plant wounding (*51*), and probably harvest periods.

Correlations between MNTs and SQTs. Total MNTs were significantly correlated to total SQTs in both leaf content and emissions (P < 0.05). Figure 2 shows the correlations between log-transformed values of MNTs and SQTs in both leaf content and emissions. Regressions of log-transformed MNT versus SQT leaf content (Figure 2a) for both herbaceous and woody species show strong correlations with slopes of 1.0 ± 0.1 and 0.83 ± 0.08, respectively. Their slopes show no statistical difference based on the ANOVA test (F = 6.74, P > 0.05), but their intercepts were statistically different (0.83 ± 0.4 and 0.98 ± 0.4, respectively, F = 1.62, P < 0.05).

At low MNT emission rates (<100 ng/(g_{DM}·h)), SQTs were the dominant terpenoids emitted, while at greater MNT emission rates (200−1500 ng/(g_{DM}·h)) emissions of MNTs and SQTs were roughly equivalent. Regressions of log-transformed MNT versus SQT emissions (T standardized at 30 °C) revealed correlations for both herbaceous and woody species (Figure 2 b). Statistical tests showed no differences between the two slopes (F = 0.46, P > 0.05) and intercepts (F = 0.43, P > 0.05); they combine to give an overall slope of 0.78 ± 0.12, an intercept of 1.6 ± 0.47, and a R^2 = 0.38 (P < 0.001). Using these empirical results, we constructed an equation to predict SQT emissions based on MNT emissions (eq 1)

$$\mathrm{BER_{SQT}} = e^{1.6} \bullet \mathrm{BER_{MNT}^{0.78}} \quad (1)$$

where $\mathrm{BER_{SQT}}$ and $\mathrm{BER_{MNT}}$ represent the basal emission rates of SQTs and MNTs, respectively, and are in units of ng/(g_{DM}·h).

This correlation is likely driven by the linkage between SQT and MNT biosynthetic pathways (*52*) as suggested by Ormeno et al. (*45*) after observation of a linear relationship between MNT and SQT emissions released by rosemary (*Rosmarinus officinalis* L.). Previous work on loblolly pine (*Pinus taeda* L.) also shows similar MNT and SQT emissions over a diurnal cycle (*53*), and measurements of α-farnesene and myrcene over a ponderosa pine forest show coincident changes in concentrations (*54*).

We compared the results for eq 1, predicting SQT emissions based on known MNT emissions, to our measured MNT and SQT values for the 22 crops (Figure 3). Figure 3 also

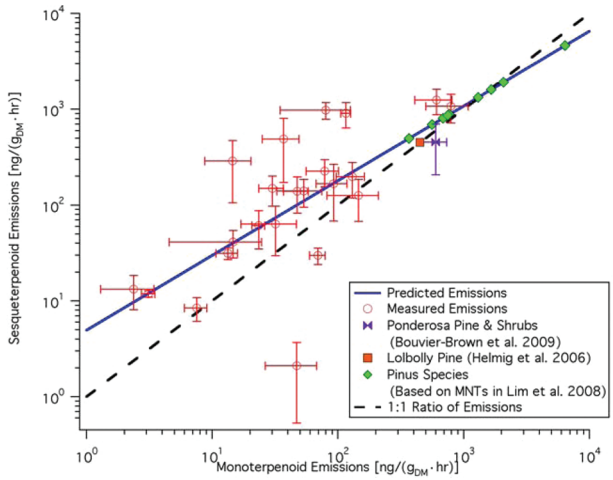

FIGURE 3. Predicted SQT basal emissions based on the average MNT basal emission rates observed (standardized at 30 °C). Measurements of MNTs and SQTS from this study are displayed with standard error bars and compared to predicted emissions based on eq 1, a 1:1 ratio of MNT to SQT emissions, and reported MNT values from literature.

TABLE 1. Statistical Analysis for Equation 1

	measured MNT and SQT emissions	
statistical measure	mean values[a]	all data points[a]
bias [ng/(g_{DM}·hr)]	−142	−148
normalized bias [%]	−3.3	24
gross error [ng/(g_{DM}·h)]	168	190
normalized gross error [%]	53	76
root mean squared error [ng/(g_{DM}·h)]	295	372
normalized rms [%]	92	135
standard error of estimate [ng/(g_{DM}·h)]	311	378

[a] Cutoff value: BER_{SQT} < 10 [ng/(g_{DM}·h).

compares eq 1 to a 1:1 SQT to MNT emissions ratio and shows the point at which MNT emissions become larger than SQT emissions (1400 ng/(g_{DM}·h)). To complement the uncertainties reported for the log−log regression, we conducted a formal uncertainty analysis (Table 1) of our predictive equation compared to the BER obtained during our measurements. This analysis of eq 1 yields a negative bias, indicating that the equation is generally underpredicting SQT emissions. The underestimation is however relatively small compared to the scale of MNT emissions as demonstrated by the small normalized biases (−3.3% and 24% for mean values and all points, respectively). The normalized root-mean-square errors shown in the same table yield 92% and 135%, when the comparison was performed using mean species values and all data points, respectively. The larger biases and errors when comparing to all data points show the significant variability in the modeled system. While our measurement and analytical techniques are prone to a significant level of uncertainty, a large portion of the error can be attributed to inherent variability in the system since significant differences in BVOC emissions exist on both a species-by-species basis and a plant-by-plant basis. In this study, we provide analyses of uncertainty from both the log−log regression and predictive eq 1 to provide a more robust evaluation and strengthen our conclusions, but we recommend further analysis once sufficient independent data becomes available.

The diversity of the species selected for this study suggests that we can confidently extend our observed correlations to other natural and agricultural species. Reported MNT emissions for numerous *Pinus* species are displayed in Figure 3 with predicted SQT emissions using eq 1. The choice of *Pinus* sp. for this analysis is based on their MNT BER, which is often within the range of the maximum values observed in the present study according to Lim et al. (*55*) and references cited therein. Our analysis is independent of large isoprene emitters (e.g., *Quercus* sp., *Populus* sp.), which in previous work were shown to have relatively small or insignificant MNT emissions (e.g. refs *56* and *57*). Given the range of reported MNT emissions from species globally and the equivalence point around 1000 ng/(g_{DM}·h), we estimate that global SQT emissions are of similar magnitude to MNT emissions; this suggests, based on a global MNT emission rate of 126 Tg/yr (*12*), that global SQT emissions are on the order of 100 Tg/yr.

This value is large compared to other recent studies but not in disagreement considering the large uncertainties associated with emission rates. Recent modeling work done using the model of Gases and Aerosols from Nature (MEGANv2.02) estimates that North American SQT emissions are 9−16% of MNTs depending on season (*18*). Their estimates are based on BERs derived from similar plant enclosure measurements and have uncertainties ranging anywhere from 2 to 5 times the reported value. They suggest that SQT emission estimates have been overestimated in the past due to preferential selection of high SQT emitters and emissions caused by plant damage (*58*). Our work suggests higher SQT emissions using a diverse selection of plants, including numerous low emitters, and paying considerable attention to avoid/filter out emissions due to plant damage. This same work using MEGANv2.02 reported that grassy agricultural crops are the second largest North American MNT emitter largely due to extensive planted acreage, which, in conjunction with our findings, reflects on the magnitude of potential SQT emissions from croplands globally (*18*). Differences between our findings and recent work testify to limited data on SQT emissions and increasing capabilities for more accurate SQT measurements. Our reasonable root-mean-square errors for both mean values and all points (92% and 135%, respectively) demonstrate suitable model performance and would suggest that future SQT emission measurements are required to better construct emission models, given the wide range of compounds we observed compared to previous studies.

We also considered the effect of seasonality on MNT/SQT emission ratios reported in recent studies. For example, SQT emissions of Scots pine (*Pinus sylvestris* L.) represent between 2 and 5% of total MNT emission rates over the year, with the exception of spring when they account for 40% (*14*). Part of this behavior is explained by SQT emissions being more sensitive to temperature than MNTs (*53*). Thus, MNTs dominate emissions of loblolly pine below 30 °C, while SQTs become dominant above 30 °C and account for twice the MNT emission rate at 40 °C (*53*). Similarly, average SQT emissions from pines have been estimated to be 9, 16, and 29% of the MNT emissions at 20, 30, and 40 °C, respectively (*30*). However, considering that the dominant fraction of terpenoid emissions occur during warm periods, the seasonal effect on relative MNT and SQT emissions does not significantly affect our ability to predict total SQT emissions.

Our emission estimate implies a much larger role for SQTs in BVOC emissions than has been previously considered during warm months. This result is in agreement with previous work suggesting that SQTs comprise a significant portion of the global BVOC budget (*59, 60*) and has particular importance for SOA formation. The formation of SOA is found to be more efficient for SQTs than MNTs in polluted air (*61*), and aerosol yields of

reactive carbon compounds range from less than 15% for some MNTs to over 80% for SQTs (*62, 63*). While significant uncertainties remain regarding SQT emission from both natural and agricultural species, correlations to both MNT emissions and leaf SQT content provide valuable methods for estimating SQT emissions on small and large scales. Given the growing evidence for importance of SQT emissions in air quality that has accompanied improved measurement techniques and enhanced knowledge about the photochemical oxidation products of SQTs, better representation of SQT emissions in BVOC emission and other atmospheric models is essential.

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Supporting Information Available

Figures (S1−S4) and tables (S1−S3) referenced in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

Literature Cited

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