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Sesquiterpene emissions from vegetation: a review

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Abstract. This literature review summarizes the environmental controls governing biogenic sesquiterpene (SQT) emissions and presents a compendium of numerous SQT-emitting plant species as well as the quantities and ratios of SQT species they have been observed to emit. The results of many enclosure-based studies indicate that temporal SQT emission variations appear to be dominated mainly by ambient temperatures although other factors contribute (e.g., seasonal variations). This implies that SQT emissions have increased significance at certain times of the year, especially in late spring to mid-summer. The strong temperature dependency of SQT emissions also creates the distinct possibility of increasing SQT emissions in a warmer climate. Disturbances to vegetation (from herbivores and possibly violent weather events) are clearly also important in controlling short-term SQT emissions bursts, though the relative contribution of disturbance-induced emissions is not known. Based on the biogenic SQT emissions studies reviewed here, SQT emission rates among numerous species have been observed to cover a wide range of values, and exhibit substantial variability between individuals and across species, as well as at different environmental and phenological states. These emission rates span several orders of magnitude (10s–1000s of ng g_{DW}^{-1} h^{-1}). Many of the higher rates were reported by early SQT studies, which may have included artificially-elevated SQT emission rates due to higher-than-ambient enclosure temperatures and disturbances to enclosed vegetation prior to and during sample collection. When predicting landscape-level SQT fluxes, modelers must consider the numerous sources of variability driving observed SQT emissions. Characterizations of landscape and global SQT fluxes are highly uncertain given differences and uncertainties in experimental protocols and measurements, the high variability in observed emission rates from different species, the selection of species that have been studied so far, and ambiguities regarding controls over emissions. This underscores the need for standardized experimental protocols, better characterization of disturbance-induced emissions, screening of dominant plant species, and the collection of multiple replicates from several individuals within a given species or genus as well as a better understanding of seasonal dependencies of SQT emissions in order to improve the representation of SQT emission rates.

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1 Introduction

Vegetation emits a vast array and substantial quantities of biogenic volatile organic compounds (BVOC), including terpenoid BVOC (isoprene, monoterpenes, sesquiterpenes) and oxygenated hydrocarbons (alcohols, aldehydes and ketones) (Kesselmeier and Staudt, 1999). BVOC play a major role in air quality, secondary organic aerosol (SOA) formation, carbon sequestration, and biospheric interactions (Atkinson and Arey, 2003). Recent studies indicate that BVOC fluxes recycle a considerable amount of photosynthetically fixed carbon to the atmosphere (Kesselmeier et al., 2002). These findings suggest that BVOC emissions estimates must be included in global carbon budget calculations and air-quality assessments. As the emissions of many BVOC are highly temperature-dependant (Guenther et al., 1993; Harley et al., 1996; Westberg et al. 2001), BVOC fluxes will likely increase during this century as a result of predicted global temperature increases (Kulmala et al., 2005; Lathière et al., 2006).

Among numerous identified BVOC, sesquiterpenes (SQT) have been among the least studied, largely because SQT analysis is challenging given the high reactivity and relatively low vapor pressure of SQT. If specific sampling protocols are not adhered to, SQT can either be lost (causing

even high SQT fluxes to be overlooked) or artificially enhanced (due to disturbances). However, several recent research projects and reviews have specifically addressed the analytical requirements for quantitative SQT emissions measurements and provide a framework for SQT measurements from enclosures and in ambient air (Komenda et al., 2001; Merfort, 2002; Helmig et al., 2003, 2004; Pollmann et al., 2005; Tholl et al., 2006).

SQT emissions are known to vary considerably between vegetation species (Arey et al., 1995; König et al., 1995; Ciccioli et al., 1999; Helmig et al., 1999, 2007; Geron et al., 2006). There are numerous other drivers controlling SQT emissions, including both biotic and abiotic factors. This literature review is presented with the objective of summarizing the current state of knowledge regarding the environmental controls governing biogenic SQT emissions. Additionally, this review contains a compendium of SQT-emitting plant species as well as the quantities and ratios of SQT these plants have been found to emit. Following a brief introduction (Sect. 1), Sect. 2 summarizes the controls (both abiotic and biotic) over biogenic SQT emissions as elucidated by numerous enclosure-based studies, sorted by individual factors (light, disturbance, etc.). Section 3 presents two tables. The first outlines some of the known SQT-emitting plant species and the quantities of SQT they have been observed to emit, while the second summarizes the ratios of individual SQT chemical species reported in various studies. Section 4 offers a brief discussion of the findings reported here and some concluding remarks.

2 Environmental controls over biogenic sesquiterpene emissions

2.1 Abiotic controls

2.1.1 Temperature

All of the studies that have examined the temperature dependencies of SQT emissions have found that emissions are highly correlated with temperature. For example, BVOC emissions from several *Citrus* varieties were found to be dominated by β-Caryophyllene (β-Car), with temperature being the main environmental control (Ciccioli et al., 1999). The investigators plotted β-Car emission data as function of leaf temperature relative to 30°C and obtained an exponential curve of normalized emissions. Based on emissions measurements from the branch of a young orange tree, Hansen and Seufert (1999) constructed a temperature-versus-emissions curve for β-Car, which showed a 5.6-fold increase in emissions for air temperature increases of 10°C. The authors suggested that perhaps there is a threshold temperature below which β-Car emissions cannot occur. Temperature experiments performed during a study of young corn plants showed that the proportion of β-Car as a percentage of total BVOC emissions was highest at 37°C (Gouinguené and Turlings, 2002). Emissions of MT and SQT from Loblolly Pine trees exhibited a strong dependence on temperature, as well as a strong diurnal SQT emission pattern with significant increases through the morning, a peak in the early afternoon, and subsequent declines into the evening (Helmig et al., 2006). SQT emissions were found to exhibit a stronger temperature dependence than MT, indicating that SQT fluxes have increased significance at high ambient temperatures (>30°C).

Comparisons between the various published SQT emissions studies are sometimes hindered by a lack of standardized emission rate (ER) reporting practices. Basal emission rates (BERs) are ERs that have been normalized to a standard temperature (usually 30°C), and are useful for making comparisons among studies. Some investigators report ERs which have been normalized according to the temperature-dependant algorithms developed by Guenther et al. (1993) for monoterpenes, or through other formulations such as the Tingey algorithm (e.g., Ciccioli et al., 1999). There have also been numerous studies in which emissions are reported as observed under various temperature and light intensities. The selection of an ER reporting approach should depend on whether emissions are obtained using relatively narrow light and temperature ranges or observed under varying temperatures and light intensities. SQT ERs are often standardized using the following exponential relationship between ER and leaf temperature (Guenther et al., 1993):

$$\mathrm{ER} = E(s)\exp[\beta(T - T(s))] \quad (1)$$

Here, ER is the emission rate (generally expressed in $\mu\mathrm{g\,g_{DW}^{-1}\,h^{-1}}$, where $_{\mathrm{DW}}$ is leaf dry weight in g) observed at temperature T, $E(s)$ is the emission rate at standard temperature ($T(s)$), and β is an empirically-derived coefficient based upon the best-fit curve obtained from plotting ln ER versus T. While some investigators normalize SQT emissions using β-factors obtained from MT emission rate studies, others derive this value empirically using SQT emissions data. Table 1 contains β-factors reported in various published SQT-related studies, as well as which compound(s) were considered in the empirical determination of this parameter and the range of temperatures used to derive this value experimentally. Calculated β-factors ranged from 0.05 to 0.29 $\mathrm{K^{-1}}$ in a single study that characterized a wide range of pine species (Helmig et al., 2007). All other studies report values that fall within this range.

2.1.2 Light

Among the studies that have examined the light dependency of SQT emissions, there have been mixed findings, with evidence that some emissions are solely temperature-controlled while others are also affected by light. However, each of the studies that did not observe light dependencies in SQT emissions were conducted in field conditions, under ambient light

Table 1. β-Factors, chemical species, and temperature range data for β-values that were determined empirically.

Compound	β-Factor (K^{-1})	Measurement temp. range, °C	Reference
Total sesquiterpenes	0.05–0.29, average: 0.17	7→43	Helmig et al. (2007)
Total sesquiterpenes	0.056–0.193 (used 0.143)	5→40	Ruuskanen et al. (2007)
β-caryophyllene	0.175, 0.201 (used 0.19)	Not given	Hakola et al. (2006)
4 different SQT	0.12–0.18, average: 0.15	4→38	Helmig et al. (2006)
β-caryophyllene	0.15 (May), 0.12 (June), 0.16 (autumn), 0.19 (early summer)	−5→32	Tarvainen et al. (2005)
Total sesquiterpenes	0.14–0.22, average: 0.19	Not given	Hakola et al. (2001)
β-caryophyllene	0.17	24→31	Hansen and Seufert (1999)
MT and SQT	0.09	12→39	Arey et al. (1995)*

*In this study, the β-factor was empirically determined using data collected from a single Monterey Pine tree, which yielded a β-value of $0.085 \pm 0.014\,K^{-1}$. Subsequently, a β-factor of $0.09\,K^{-1}$ was used to normalize emissions of total MT+SQT for all MT/SQT-emitting species that were screened.

and temperature regimes. As noted by Hakola et al. (2006), it can be difficult to discern light dependencies from emissions data collected during field experiments, where measurements may be performed under light-saturated conditions. Much of the literature suggests that dependencies on temperature are much stronger than those for light (e.g., Helmig, 2006).

β-Car emissions from sunflower were observed to be both light- and temperature-dependent (Schuh et al., 1997). By varying light intensity, but not temperature, the investigators constructed a light-dependent curve for β-Car emissions. At a constant leaf temperature of 23°C, β-Car emission was invariable at PPFDs between 0 and $275\,\mu mol\,m^{-2}\,s^{-1}$; but emission roughly doubled each time PPFD was increased by $275\,\mu mol\,m^{-2}\,s^{-1}$ up to a threshold of $825\,\mu mol\,m^{-2}\,s^{-1}$. When PPFD was adjusted from 825 to $1100\,\mu mol\,m^{-2}\,s^{-1}$, the emission of β-Car only increased by ∼50%. In this study, emissions were detected at night (at low levels), and it was suggested that these could be attributed to simple diffusion from storage pools (a temperature-dependent process). The investigators ruled out stomatal control as a factor affecting the BVOC flux after experimenting with varying degrees of stomatal conductance. The authors concluded that BVOC emission rates from sunflower depend both on biosynthesis rates as well as diffusion out of pools. In Downy Birch, Hakola et al. (2001) found that SQT emissions continued after light was prevented from reaching branches.

β-Car emissions from the branch of a young orange tree were not detected in the dark even when temperatures were comparable to those under lighted conditions (Hansen and Seufert, 1999). In a later study, Hansen and Seufert (2003) analyzed the β-Car emissions data from Ciccioli et al. (1999) using two algorithms to determine whether observed emission rates were better modeled using a temperature-only or a light- and temperature-based algorithm. The algorithm that assumed both light and temperature dependencies produced modeled data points that more closely matched observations than values obtained by assuming emissions were solely temperature-dependent. However, Ciccioli et al. (1999) reported that emission rates were similar for branches growing in full versus half-shaded areas, and concluded that β-Car emissions were unaffected by varying stomatal conductance.

Young corn plants were found to emit several SQT chemical species which responded differently to changing PPFDs (Gouinguené and Turlings, 2002). Under constant chamber temperatures β-Car emissions were positively correlated with light intensity, α-farnesene and β-bisabolene were negatively correlated, and other SQT species were unaffected by changing light levels. Under increasing light-intensity conditions, significant increases in total induced BVOC emissions occurred, while relative contributions from α-farnesene and β-bisabolene to total emissions declined. β-Car increased from about 1.3% to 2.8% of total BVOC emissions when illuminance changed from 0–$5000\,lm\,m^{-2}$. The investigators noted that emissions responded sharply to changes in light-dark cycles, an indication that circadian rhythms were not controlling these releases (see Sect. 2.1.5).

Tomato shoots exposed to perpetual light exhibited continuous emission of α-copaene (Maes and Debergh, 2003). During this experiment, the emission of β-Car declined, while levels of α-copaene increased until they exceeded those of β-Car, a behavior not observed under unstressed (i.e., normal light-dark phase) conditions. When the emission profile of α-copaene (for an unstressed tomato shoot) was examined, a clear diurnal emission pattern was evident,

with an increase during the day and a decline at night. The investigators suggested that α-copaene requires light for its biosynthesis and/or emission. During the continuous light experiments, temperature inside the experimental room was maintained at 27°C, and PPFD was constant at 70 μmol m^{-2} s^{-1}. A biotic stressor (caterpillar herbivory) was also applied to tomato shoots, and elevated levels of SQT were observed (see Sect. 2.2.3). In Scots Pine, β-Car was the dominant SQT, emitted at levels representing 2–5% (southern Finland) and 40% (northern Finland) of measured springtime MT emissions (Tarvainen et al., 2005). SQT emissions were not found to be light-dependent, and appeared to vary seasonally (see Sect. 2.1.4).

Though Helmig et al. (2006) concluded that light influenced SQT emissions from Loblolly Pine, the variables of light and temperature were difficult to separate given the ambient conditions observed during the course of their study. Despite this, the authors found the best fit of modeled data to observed values when SQT emissions were assumed to be 20% temperature-only and 80% light- and temperature-dependent. The BVOC emissions of 40 year-old Scots Pine trees were studied under varying temperatures and light intensities and over changing seasons (Holzke et al., 2006). Standardized emissions algorithms (after Guenther et al., 1993) were computed to evaluate emission rate dependencies on light and temperature. SQT accounted for up to 6% of total measured BVOC emissions, but had a strong seasonal variation (see Sect. 2.1.4). Despite the fact that emissions were not detected at night, the effects of light were not found to be significant.

2.1.3 Diurnal emission patterns

All studies involving volatile collection at multiple times during the day report diurnal rhythmicity in SQT emissions. When Black Sage (*Salvia mellifera*) plants were sampled throughout the day, total emission rates (and SQT emission rates in particular) were higher in samples obtained earlier in the day (Arey et al. 1995). Since there was a relatively narrow temperature range recorded during the course of this study, one explanation given for the daily decline in SQT emissions is that there are limited storage pools which are depleted each day, a finding that parallels previous observations made on MT emission rates for Black Sage (Dement et al., 1975). In the Arey et al. study, ten native plant species representing significant sources of biomass within the South Coast Air Basin of California were screened for BVOC emissions, and three of these species (Black Sage, California Sagebrush, and Greenbark) emitted SQT.

Volatile emissions from developing rose flowers obeyed a diurnal, circadian pattern when the effects of altered light-dark regimes were tested (Helsper et al., 1998). During a 12-h photoperiod experiment, SQT emissions tended to peak 6–9 h into the photoperiod, but never dropped off completely even in dark periods. β-Car was not emitted during a 5-day period of extended darkness, though β-cubebene emissions were observed to increase during this time. When flowers were exposed to a 12-h photoperiod, followed by either continuous light or continuous darkness, emission rhythmicity in both cases was found to continue for two or three cycles and then gradually decrease. The authors postulated that observed rhythmicity has a biochemical, and not a physical (e.g., petal closure) basis, and that emission of β-Car is light-dependent. In a study of snapdragon flowers, rhythmicity of the nonmevalonate (i.e., MEP) pathway was found to affect nerolidol biosynthesis and emission more directly than light, although it was also noted that in these flowers both processes occur in non-photosynthetic cells (Dudareva et al., 2005).

β-Car emissions from various *Citrus* varieties increased during the morning and generally peaked around noon (Ciccioli et al., 1999). Stomatal closure was not found to affect emissions, as β-Car (and several monoterpenes) was detected at night, and no correlation was observed between BVOC emissions and uptake of CO_2.

Major compounds released by both young and mature potato plants during morning, noon, and afternoon hours were quantified to characterize diurnal rythmicity of emissions and emission variability among individual plants (Agelopoulos et al., 2000). Investigators also looked for a relationship between foliage weight and emissions for both young and mature plants. Potatos were found to emit predominantly SQT, and the composition of emitted compounds was constant during the photoperiod and between young and mature plants. Quantities of emitted SQT increased steadily throughout the day and peaked in the afternoon for both young and mature plants, except for the release of an unknown compound (from young plants) which was emitted at relatively constant amounts all day (see Sect. 2.2.1).

Herbivore-induced nighttime BVOC emissions of tobacco plants were studied based on the hypothesis that selected species of ovipositing female moths are repelled by herbivore-infested plants which emit these volatile blends as a result of herbivory (see Sect. 2.2.3) (De Moraes et al., 2001). Several non-SQT compounds which were not present in the daytime samples were detected at night. SQT were emitted both during the day and night, but emission rates were 1.2–3 times higher in the daytime. Release of germacrene-D from forest tent caterpillar-infested poplar leaves exhibited a diurnal rythmicity with emissions maxima occurring during the photoperiod (06:00–18:00 h) and extremely low (often undetectable) quantities detected during dark periods (Arimura et al., 2004). In an ambient study of Siberian Larch, diurnal fluctuations of SQT and MT emissions were attributed to temperature variations (Ruuskanen et al., 2007).

2.1.4 Seasonality

Some studies indicate that seasonality can be as important as temperature in exerting control over biogenic SQT release, while others have determined that emissions can be adequately described by temperature alone. When Black Sage plants were monitored in the field (between mid-February and December), changes in the ratios of SQT emissions (as proportions of total emitted BVOC) comprised the largest change in emission profiles (Arey et al., 1995). The investigators suggested that perhaps the phenological state of the Black Sage controls SQT production, as this was observed to be higher prior to the peak blooming of the plants in May, or that the high SQT production was a response to aphid infestation (see Sect. 2.2.3). The authors did not believe that enhanced SQT ratios were caused by ambient temperatures, since proportions were low in August (when temperatures were high) and high in December (when night temperatures were low). The authors concluded that overall, there was not a significant seasonal dependence of BVOC emissions, but that disturbances to the plants may have exerted the most influence on total observed emission variability.

BVOC emissions within a *Citrus* orchard in Spain were measured during April–May, July, and again in October. β-Car was the dominant BVOC emitted by 6 different *Citrus* varieties during July sampling, comprising 50–70% of all detected hydrocarbons, but total emission rates varied by up to one order of magnitude between cultivars (Ciccioli et al., 1999). Emissions of all BVOC were negligible during October. The authors noted that SQT are thought to be synthesized outside of chloroplasts and stored in pools. For samples collected from April to May, when temperatures were 5–10°C lower than average July temperatures, a dramatic reduction in β-Car emissions was observed.

Several species of deciduous trees exhibited significant changes in BVOC emissions between June and August (Zhang et al., 1999). Since light and temperature regimes were nearly the same during these two months, the authors attributed these changes to leaf maturation. Higher emissions were observed at higher temperatures, however. For β-Car, emissions rose sharply between 16 and 24°C, then plateaued. Temperatures recorded for June sampling were similar to those recorded during August. Downy Birch emitted by far the highest quantities and largest number of SQT and oxygenated SQT. Among these, β-Car, caryophyllene oxide, and α-copaene were emitted in the greatest quantities. In June, bourbonene, α-copaene, and β-Car were among the major compounds detected from European Birch. Trembling Aspen and Black Elder emitted fewer SQT than the birch species. For August samples from all four species, fewer SQT were detected, and at lower levels than those recorded in June. An exception was muurolene, which was released by European Birch at higher levels in August than in June.

Measurements from Scots Pine were taken from early spring through autumn in southern and northern Finland (Tarvainen et al., 2005). β-Car emissions exhibited significant seasonal variability, with maximum emissions observed during summer months. A similar trend was observed for this species by Hakola et al. (2006), who found that the highest emissions potentials for β-Car and other SQT (after being normalized to 30°C) occurred in July.

When emissions from two Silver Birch trees were measured in July and August, July emissions were SQT-dominated, with SQT comprising 39–71% of total BVOC, while August samples were MT-dominated, with SQT making up 16–36% of total emissions (Vuorinen et al., 2005; also see Sect. 2.1.5).

Standardized SQT ERs varied seasonally in Siberian Larch, with α-farnesene dominating the ∼12% contribution of SQT to total summertime BVOC emissions. In the fall, SQT comprised only ∼3% of emitted BVOC, and the percent contribution of α-farnesene to total SQT also fell significantly (Ruuskanen et al., 2007).

The fractional contribution of SQT to total BVOC emissions from Scots Pine displayed a strong seasonal variation, with much higher percentages of SQT (up to ∼6% of total terpene emissions) found in the spring/early summer than were measured in August-October (Holzke et al., 2006). The authors noted that this strong seasonal SQT variability could create unique chemical regimes during different seasons. Investigators also observed that light and temperature variability alone did not explain the observed trends and that both endogenous (e.g., developmental stage of branch) and exogenous (e.g., temperature) factors were likely responsible for the variability observed during the course of the year. The authors suggested the development of emissions algorithms incorporating both physiological and ontogenic parameters in order to better predict BVOC fluxes.

2.1.5 Other abiotic factors

Light and temperature are not the only abiotic drivers of variability in SQT emissions. Soil moisture and air humidity, plant water stress, and fertilization levels can also contribute to changes in SQT fluxes, while trace gas concentrations (CO_2, O_3) appear to have less impact on observed variability. The effects of water stress on terpenoid emissions from the branch of a young orange tree were investigated by Hansen and Seufert (1999). Samples were collected at roughly the same time each day. β-Car accounted for a significant portion (40–45%) of total emissions. Severe drought reduced β-Car emissions to <6% of pre-drought levels, but emissions were unaffected by mild drought conditions. Similarly, Ormeño et al. (2007b) observed reduced SQT emissions following drought stress in Rosemary, Kermes Oak, Aleppo Pine, and Rock Rose.

Induced BVOC emissions from young corn plants were studied under varying soil moisture, air humidity, temperature, light intensity and rhythm, and at different fertilization rates (Gouinguené and Turlings, 2002). All factors were

tested independently of each other. Emissions were induced after application of caterpillar oral secretion, which was either directly injected into stems or applied to leaves that had been mechanically damaged. Generally, the plants did not emit significant levels of BVOC when they were undamaged, irrespective of the abiotic stressor applied. In the presence of herbivore wounding, however, the plants emitted several SQT and the quantities and ratios of these compounds were affected by all abiotic stressors. The investigators noted a negative relationship between soil moisture and induced emissions. However, two SQT were shown to increase in terms of their fractional contribution to emissions as soil moisture increased. Induced emissions were highest at relative air humidities between 45% and 65%, and no humidity-related effect was observed on the composition of odor blends. Fertilization rate negatively affected induced emissions, even when these were normalized to plant biomass. Percentages of the SQT α-bergamotene and (E)-β-farnesene did not change when fertilization rates were varied, however. Certain SQT compounds appeared to be less sensitive to changes in various abiotic factors than other compounds.

SQT emissions from Rosemary, Aleppo Pine, and Rock Rose did not vary according to soil nutrient content when emissions from these species were studied across siliceous and calcareous soils (Ormeño et al., 2007a). Exceptions are the standardized emissions of α-humulene from Aleppo Pine, which was higher in specimens growing in calcareous soils, and of α-humulene and β-bourbonene from Rock Rose, which were higher in specimens growing in siliceous soils. Despite the general lack of correlation between SQT emissions and soil type, SQT emitted from both Rosemary and Aleppo Pine comprised a higher percentage of total BVOC emissions in plants growing in siliceous soils.

The effects of elevated ($\sim$2$\times$ambient) CO_2 on induced emissions of cabbages (which included the SQT α-farnesene) subjected to insect herbivory were examined by Vuorinen et al. (2004). The results suggested no statistically significant effect on induced SQT emissions from plants grown under these conditions. In another study, BVOC emissions from two Silver Birch clones grown under ambient and elevated CO_2 and at varying O_3 concentrations were measured (Vuorinen et al., 2005). The variables were tested separately as well as in concert, and results indicated that elevated atmospheric concentrations of CO_2 and O_3 do not significantly affect emissions of MT or SQT from this species.

2.2 Biotic controls

2.2.1 Plant developmental stage

Numerous authors have noted that the release of SQT appears to vary not only according to light and temperature intensity, time of day, and season, but is also determined by the phenological state of a plant (e.g., leaf age, blossoming). During BVOC sampling of several *Citrus* cultivars, multiple cuvettes were placed within a given tree in order to ascertain the effects on emissions from immature fruits, sun/shade regimes, and the presence of flowers (Ciccioli et al., 1999). The presence of semi-mature fruits within some enclosures did not have a significant effect on overall emissions. During springtime (April–May) sampling, many of the branches contained blossoms, and total emissions from flowering branches were approximately an order of magnitude higher than emissions from non-flowering branches. Furthermore, these emissions were not dominated by β-Car, but instead by MT. Hansen and Seufert (1999) found that emissions from the branch of an orange tree that contained blossoms had terpene emissions almost eight times higher than samples collected after the removal of blossoms. However, SQT accounted for a similar percentage of the total terpene emissions from the branch irrespective of whether or not flowers were present.

Ratios of total SQT emissions to β-farnesene were relatively stable in both young and mature potato plants, though variability in quantities of SQT emissions was highest (varying by up to an order of magnitude) among young plants (Agelopoulos et al., 2000). Mature plants exhibited a greater correlation between foliage weight and emissions than young plants. The BVOC emission rates of young trees from two birch species were quantified over the course of a growing season in experiments by Hakola et al. (2001). One species, Silver Birch (*B. pendula*), did not emit SQT, while Downy Birch (*B. pubescens*) did. Three years after their first measurements, the authors again studied emissions from *B. pubescens*, this time using older trees. Mature *B. pubescens* emitted higher proportions of SQT than younger trees, and at greater quantities. Emissions data following leaf initiation in the spring were analyzed as a function of Effective Temperature Sum (ETS) and presented in terms of ranges of degree days (d.d.). SQT emissions potentials for *B. pubescens* appear to be highest between 400–800 d.d.

2.2.2 Disturbance

Disturbances to vegetation during enclosure set-up have been observed to cause significant bursts in SQT emissions. Arey et al. (1995) noted that when Black Sage plants were not handled carefully during enclosure set-up, disturbance-related emissions bursts occurred which were roughly an order of magnitude higher (up to 205 $\mu g\, g_{DW}^{-1}\, h^{-1}$) than reported averages. However, ratios of individual compounds did not change much. Hakola et al. (2001) also observed that rough handling caused temporary but significant increases in emissions from birch trees.

The potential for artificially increasing emission rates during the setup of the enclosure system was not realized until relatively recently. As researchers began paying more attention to this effect, enclosure techniques have been improved. Researchers will now typically wait a considerable time ($\sim$12–24 h) after installation of the enclosure and prior

Table 2. Compendium of studies of biogenic SQT emission, plant species used in each study, the quantities and qualities of SQT emitted, and whether or not reported ERs can be considered quantitative.

Reference	Plant Species	Chemical Species	Emission Rates (ERs)				Remarks	Quantitative?
			ng g_{DW}^{-1} $hour^{-1}$	ng hr^{-1} biomass not reported	ng m^{-2} hr^{-1}	SQT % of total BVOC		
Agelopoulos et al., 2000	Potato plants; *Solanum tuberosum* L. cv. Desireé	β–Car		609-1276		38-46	1	Semi
		(E)-β–farnesene		256-561		16-20		
		(Z,Z)α–farnesene		103-250		6-10		
		germacrene-D		208-441		13-15		
		β–bisabolene		179-436		11-14		
		unknown compound		77-189		4-7		
Arey et al., 1995	Black Sage (*Salvia mellifera*)	α-cubebene α-copaene β-bourbonene β–Car germacrene-D	<20-5600 field 286-2272 greenhouse (gh)			<1-70 field 1.3-7.1 (gh)	2	Yes
	Greenbark	Not stated						
	California Sagebrush	Not stated						
Arimura et al., 2004	Hybrid Poplar (*Populus trichocarpa* **x** *deltoides*)	germacrene-D	80 (a), 10 (b), 0 (c)				3	Yes
		(*E*,*E*)-α-farnesene	60 (a), 30 (b), 0 (c)					
Chen et al., 2003	Thale Crest (*Arabidopsis thaliana*, Columbia ecotype)	β-Car		~11.5		~44	4	Semi
		thujopsene		~1.25		~5		
		α-humulene		~0.9		~3		
		β-chamigrene		~0.75		~3		
		β-farnesene		~0.6		~2		
		cuparene		~0.25		~1		
Ciccioli et al., 1999	Varieties of *Citrus sinensis* and *Citrus Clementi* sampled during July	β–Car (Valencia Navel)			~36000	50-70	5	Yes
		β–Car (Valencia Navel-late and Clemenule)			180000-360000	50-70		
		α-humulene				<1		
Degenhardt and Lincoln, 2006	Marsh Elder (*Iva frutescens*)	germacrene-D			9200-15000	~6	6	Yes
		β–Car			1000-11000	1-4		
		α-humulene			1000-2000	~1		
		cis-β–guaiene			0-8000	0-5		
De Moraes et al., 2001	Tobacco (*Nicotiana tabacum*)	β–Car		3741 (a) 1227 (b)		~46.6 (a) ~23.5 (b)	7	Semi
		α–farnesene		610 (a) 445 (b)		~7.6 (a) ~8.5 (b)		
		α–humulene		111 (a) 42 (b)		~1.4 (a) ~0.8 (b)		
		unidentified SQT		574 (a) 481 (b)		~7.2 (a) ~9.2 (b)		
Dudareva et al., 2005	Snapdragon flowers (*Antirrhinum majus* cv. Maryland True Pink)	nerolidol	~200-4000***			~45-65	8	Semi
Gouinguené and Turlings, 2002	Corn (*Zea mays*)	β–Car	Widely-varying emission rates for all compounds; none explicitly stated			0.7-15	9	No
		α-bergamotene				7.5-40		
		β–farnesene				0-40		
		α–farnesene and/or β–bisabolene				0.5-2.8		
		(E)-nerolidol				0-2.5		
Hakola et al., 2001	Downy Birch (*Betula pubescens*)	*cis*–caryophyllene β–Car α–farnesene	310-6940			<5-~75	10	Yes
Hakola et al., 2006	Scots Pine (*Pinus sylvestris* L.)	β–Car	11(a), 171(b), 42(c), 15(d)			0-26	11	Yes
		Other SQT	1(a), 39(b), 19(c), 7(d)			0-6		

Table 2. Continued.

Hansen and Seufert, 1999	*Citrus sinensis* (L.) OSBECK	β–Car (normal conditions)	410			40-45	12	Yes
		β–Car (varying water stress)	20-410					
Helmig et al., 1999	Ironwood	Total SQT	800			14.8	13	Semi
	Post Oak	Total SQT	78000			48.8		
	Black Oak	Total SQT	8500			11.2		
	White Oak	Total SQT	2600			3.2		
	Speckled Alder	Total SQT	300			1.8		
	Black Cherry	Total SQT	3800			34.5		
	Red Raspberry	Total SQT	73000			35.3		
	White spruce	Total SQT	1500			2.5		
	Eastern Hemlock	Total SQT	100			0.9		
	Labrador Tea	Total SQT	14000			21.5		
	Subalpine Fir	Total SQT	800			5.0		
	Aspen	Total SQT	300			1.1		
	Big Sagebrush	Total SQT	1300			4.2		
	Englemann Spruce	Total SQT	<100			<2.4		
	Lodgepole Pine	Total SQT	300			0.6		
	Gambel Oak	Total SQT	1500			2.2		
	Rabbit Brush	Total SQT	3200			2.9		
	Salt Bush	Total SQT	15000			31.3		
Helmig et al., 2006	Loblolly Pine (*Pinus taeda* L.)	β–Car	297			~50	14	Yes
		α–bergamotene	54					
		α–humulene	45					
		β-farnesene	50					
Helmig et al., 2007	Gray Pine (*Pinus sabiniana*)	Total SQT	60 (greenhouse)			1.5	15	Yes
	Scots Pine (*Pinus sylvestris*)	Total SQT	<4 (greenhouse)			0.0		
	Ponderosa Pine (*Pinus ponderos*)	Total SQT	70 (July and August)			12.3		
	Shortleaf Pine (*Pinus echinata*)	Total SQT	90 (September)			37.5		
	Beach Pine (*Pinus contorta)*	Total SQT	100 (September)			37.0		
	White Pine (*Pinus strobus*)	Total SQT	100 (June, July)			11.9		
	Red Pine (*Pinus resinosa*)	Total SQT	80 (July)			11.6		
	Loblolly Pine (*Pinus taeda*)	Total SQT	150, 350 (August, September)			46.9, 42.7		
Helsper et al., 1998	*Rosa hybrida* L. cv. Honesty (flowers)	β–Car		100		0.4	16	Semi
		β-cubebene		350		1.4		
Holzke et al., 2006	Scots Pine (*Pinus sylvestris* L.)	γ-cadinene	0.64, 5.94, 0.93, 0.02				17	Yes
		δ-cadinene	0.31, 5.26, 1.24, 0.01					
		α-muurolene	0.20, 3.83, 0.68, <0.01					
		Aromadendrene	0.17, <0.01, 0.16, <0.01					
		β–Car	0.66, 26.20, 1.66, 0.01					
		β–cedrene	0.46, 31.23, 5.49, 0.07					
		β-bourbonene	0.14, 0.49, 0.05, <0.01					
		α-ylangene	0.16, 0.31, 0.14, <0.01					
König, et al., 1995	Hornbeam (*Carpinus betulus*)	β–Car	20.3			12.6	18	Yes
	Birch (*Betula pendula*)	other SQT	61.2			11.0		
Martin et al., 2003	Norway Spruce (*Picea abies* L. Karst)	α-bergamotene	(a) 0.0* (b) 10.5*			0, 0.2	19	Yes
		β-farnesene	(a) 26.7* (b) 2653.4*			4.3, 55.1		
		α-farnesene	(a) 29.4*, (b) 46.8*			4.7, 1.0		
		α-bisabolene	(a) 62.9* (b) 972.3*			10.1, 20.2		
		other SQT	(a) 0.0* (b) 10.5*			0, 0.2		
Ormeño et al., 2007a	Rosemary (*Rosmarinus officinalis* L.)	α-humulene α-muurolene 2 unidentified SQT β-Car	~300-400			5-15	20	Semi
	Aleppo Pine (*Pinus halepensis* Mill.)	α-humulene α-muurolene β-bourbonene copaene β-Car 2 unidentified SQT	~200-500			6-23		

Table 2. Continued.

Ormeño et al., 2007a (cont.)	Rock Rose (*Cistus albidus* L.)	AR-curcumene α-zingiberene β-bourbonene β-Car α-humulene allo-aromadendrene copaene α-muurolene 2 unidentified SQT	~2200-3000			~76		
Ormeño et al., 2007b	Rosemary (*Rosmarinus officinalis* L.)	allo-aromadendrene	~405			5.8	21	Yes
		germacrene-d	~475			6.8		
		α-zingiberene	~500			7.13		
		d-cadinene	~525			7.5		
	Aleppo Pine (*Pinus halepensis* Mill.)	α -humulene	~20			5.3		
		allo-aromadendrene	~35			9.8		
		germacrene-d	~20			6.5		
		d-cadinene	~25			7.7		
	Rock Rose (*Cistus albidus* L.)	β-bourbonene	~155			7.0		
		β-Car	~150			6.8		
		α -humulene	~15			0.7		
		allo-aromadendrene	~150			6.7		
		germacrene-d	~145			6.6		
		AR-curcumene	~235			10.7		
		α-zingiberene	~245			11.1		
	Kermes Oak (*Quercus coccifera* L.)	allo-aromadendrene	~85			5.4		
		germacrene-d	~70			4.5		
		d-cadinene	~140			8.9		
Ruther and Kleier, 2005	Corn (*Zea mays* cv. Delprim)	(E)-β–farnesene	0.25***			6	22	Semi
		sesquithujene	0.2***			5		
		β–Car	0.1125***			3		
		(E)-α-bergamotene	0.0875***			2		
		β–bisabolene	0.0125***			<1		
		7-epi-sesquithujene	0.0125***			<1		
Ruuskanen et al., 2007	Siberian Larch (*Larix sibirica*)	α-farnesene	0.958-1.798 (a)			~10 (a) ~1 (b)	23	Yes
		β-Car longifolene β –cubebene s-cadinene α –humulene β-bourbonene iso-longifolene	0.404-0.596 (b)			~2 (a) ~2 (b)		
Schuh et al., 1997	Sunflower (*Helianthus annuus* L. cv. giganteus)	β–Car	93-303			~26	24	Yes
		α-humulene	9.9-38			~3		
Tarvainen et al., 2005	Scots Pine (*Pinus sylvestris* L.)	β–Car	<4.5-37, 160-533, 0-158			0-2, 3-26, 0-4	25	Yes
		unidentified SQT						
Vuorinen et al., 2005	Silver Birch (*Betula pendula* Roth)	α–copaene (July)	278-1498**			~5-8	26	Yes
		α–copaene (August)	10-65**			~2-3		
		β–Car (July)	224-1184**			~3-4		
		β–Car (August)	4-54**			~1-2		
		α-farnesene (July)	91-991**			~2-11		
		α-farnesene (August)	13-326**			~1-12		
Zhang et al., 1999	European Birch	Total SQT	25-211, 12-60			~20, 11	27	Semi
	Downy Birch	Total SQT	663-1494, 204-363			~22, 9		
	Trembling Aspen	Total SQT	132-632, 0-11			~41, 19		
	Black Elder	Total SQT	2-62, 1-13			~22, 17		

to sample collection to allow initial bursts of emissions to subside. Many of the early published SQT ER studies may have reported artificially elevated ERs caused from the rough handling of vegetation specimens and premature sample collection. Observed emissions changes due to artificial disturbances in enclosure experiments suggest that emissions bursts might also be caused in nature by natural disturbances (e.g. violent weather events), but this potential effect has yet to be characterized and published.

2.2.3 Infestation

Among the known BVOC chemical species, many SQT play critical roles in plant-insect and plant-plant interactions. For instance, Turlings et al. (1995) studied the release of SQT and other BVOC by corn seedlings as a response to caterpillar feeding, and demonstrated that their emissions attracted wasps which parasitize caterpillars. In another study, tobacco plants were shown to emit herbivore-induced BVOC (including SQT), which repel ovipositing female moths, thus

Table 2. Footnotes.

* ERs were published as ng $g^{-1}_{freshweight}$ h^{-1}. For coniferous tree species, the ratio of fresh to dry weight is ∼1.5–2.5. Therefore, the ERs listed may be a factor of 1.5–2.5 lower than what would have been reported if dry weight had been used.
** ERs were published as ng $g^{-1}_{freshweight}$ h^{-1}. For deciduous tree species, the ratio of fresh to dry weight is ∼2–3. Therefore, the ERs given in this study may be a factor of 2–3 lower than what would have been reported if dry weight had been used.
*** ERs were published as ng $g^{-1}_{freshweight}$ h^{-1}. For non-tree vegetation, the ratio of fresh to dry weight can vary considerably. Therefore, the ERs reported here cannot be quantitatively scaled to ng g^{-1}_{DW} h^{-1} without fresh:dry weight ratio data for the plant specimens used in this study.
Remarks: This information is presented as: Experimental conditions, sample dates, # of specimens measured, # of replicates per specimen. In cases where experiments were performed in a laboratory or greenhouse, the word "lab" is given instead of listing sample dates. For all items, "n.s." appears if this information was not stated.

1. ERs represent mean emissions ranges from whole plants. Samples were collected at temperatures between 16–19°C and at an illuminance of 1500–1600 lm m^{-2}. These ERs were not normalized for biomass, though plants within each group were similar in weight, lab, ∼84, 1.
2. Emissions were normalized to 30°C. Large volume flow-through plant enclosure chamber with high air flow (∼40 LPM) of charcoal-scrubbed medical-grade air (ambient [CO2]). Whole plants were enclosed. Enclosures were allowed 20–30 mins of equilibration time. For California Sagebrush, substantial variability in emission profiles was observed between individual plants; the authors felt that disturbances of glandular trichomes on leaf surfaces may have influenced these emissions, for Black Sage in field: April–October, 7, 6–21, for Black Sage in greenhouse: lab, 3, 5–6.
3. Trees were maintained in a greenhouse under summer conditions (daytime temperatures: 18.3–21.8°C; relative humidity: 24.5–47.2%). ERs are given for (a) FTC-infested trees after 24 h of feeding, (b) trees damaged by mechanical wounding, and (c) undamaged control trees. All emissions were recorded from directly-damaged leaves (non-systemic leaves), lab, 5, 1.
4. 6-week-old whole plants were sampled at 23°C and 150 μmol m^{-2} s^{-1} PAR using dynamic enclosures purged with purified air. 8-h samples were collected, and listed ERs represent hourly averages per whole plant, lab, 5, 4.
5. ERs were normalized to 30°C and 1000 μmol m^{-2} s^{-1}PPFD. Temperatures within the enclosures were maintained within 2–3°C of ambient temperatures. Ozone was reduced to <10% of ambient levels, July, *C. sinensis*: 5, n.s.; *C. clementi*: 1, n.s.
6. Volatiles were collected at 22°C. Enclosure was purged with compressed medical-grade air, lab, 12, 1–10.
7. Average emission rates given for approximately (a) noon, 50 h after initial herbivore damage, and (b) 08:00 p.m., 58 h after damage. 8-week-old plants were sampled at 29±4°C, lab, n.s., n.s.
8. Experiments were conducted using cut 5-d-old flowers. ERs reflect the range observed across light (150 μmol m^{-2} s^{-1} PAR) and dark periods under a constant air temperature of 21°C, lab, 3, 2–3.
9. ERs depended on abiotic factor being tested and whether or not plant was damaged, lab, >60, 1–12.
10. ERs were standardized to 30°C. Air was scrubbed of ozone (using MnO_2-coated copper nets) before being flown into enclosure, n.s., 18, n.s.
11. ERs were standardized to 30°C and are calculated as averages from sunlit branches for (a) April–May, (b) June–July, (c) August, and (d) September–October. Enclosure inlet air was ozone-scrubbed, April–October, 1, 2.
12. ER associated with non-drought conditions for cuvette air temperatures of 30°C and PPFD of 1069 μmol m^{-2} s^{-1}. Water stress ERs depended on level of stress, cuvette air temperatures were 29–31°C at PPFDs of 1016–1095 μmol m^{-2} s^{-1}. Purge air was scrubbed, lab, 1, 1–20.
13. Emission rates were normalized to 30°C using response curves developed from MT. Hydrocarbon-free air was flown into enclosures. 63 vegetation species from 3 distinct sites (each investigated during a different period of the summer) in the US were screened for BVOC emissions. Healthy, sunlit branches were cut from trees and samples were collected after the enclosures had been allowed to equilibrate for 10 min. Most of the emission data obtained during this experiment were collected under relatively constant light and temperature values around 40°C and 1700 μmol m^{-2} s^{-1} PPFD. ∼25 separate SQT were observed, though individual SQT were not speciated in this study. Errors were stated to have been within a factor of 2-3 based on adverse enclosure conditions due to higher-than-ambient temperatures inside of enclosures, possible disturbances to branches, and analytical uncertainties, June–August, 1–4, 1.
14. ER was normalized to 30°C. Individual SQT temperature-dependent emissions curves were also presented. Enclosures were allowed to equilibrate for ∼1 d prior to sampling. Purge air was scrubbed. Needle temperatures were recorded. Uncertainty in SQT ER was stated as ±15%, Late September, 4, 10–34.
15. Total SQT ER represents BER, normalized to 30°C. SQT emissions were found in 7 of 8 pine species screened. Measurements were conducted during different months depending on species. Enclosures were allowed to equilibrate for ∼0.5–1 d prior to sampling. Purge air was scrubbed. Needle temperatures were recorded, March-September, 1–4, 1-34.

Table 2. Footnotes continued.

16. Temperature was kept constant at 20°C, with a relative humidity of 75% and a constant PPFD of 210 μmol m^{-2} s^{-1}. Petal temperature was monitored by attaching a thermocouple to outer petals of flowers, lab, 3, 1.
17. ERs were normalized to 30°C. The four numbers reported for each compound represent average daytime emissions for March-Apr., May, June-July, and Aug.-Oct. Nighttime measurements showed non-detectable emission levels. Enclosure air was VOC and O_3-scrubbed. Enclosures equilibrated overnight prior to sample collection, March–October, 2, ∼50.
18. Of nine agricultural and natural species studied, only two were found to be SQT emitters; Hornbeam and Birch. Aside from β-Car, other SQT were not speciated. Enclosure temperatures were ∼23°C. Ambient air was charcoal-scrubbed, sampling began 20 mins after plants were enclosed, minimal disturbance to plants was emphasized, Mid-May, 1 (per species), 1–2.
19. All experiments were conducted at a constant temperature of 22°C, 75% relative humidity, and at a PPFD of 350 μmol m^{-2} s^{-1}. SQT ERs (and SQT % of total BVOC emissions) reported for both (a) untreated control plants and (b) plants ∼24 h after being treated with methyl jasmonate, lab, 3, 1.
20. Samples were collected between 11:00–15:30 (solar time). ERs listed are non-standardized means and represent ranges observed across plants growing in siliceous and calcareous soils. Sun- and shade-exposed twigs were sampled. Ambient temperatures during sampling were 22–25°C and PAR ranged from 750–960 μmol m^{-2} s^{-1}. Enclosures were semi-dynamic and were set up ∼10 min prior to sampling. Inlet air was pollution-free, late March, 24 (per species), 1.
21. Healthy sun- and shade-exposed twigs were sampled. ERs given in Table 2 reflect those of unstressed plants and were standardized to 30°C. Ambient temperature was ∼32°C (enclosure temperatures were not reported), PAR was ∼1310 μmol m^{-2} s^{-1}. Enclosures were set up and purged with zero air beginning 15 min prior to sampling, early June, 6 (per species), 1.
22. Enclosure air was charcoal-scrubbed. Volatiles were collected for an 8-hour period; the ERs listed in Table 2 were divided by 8 to give average ERs per hour, lab, 9, 1.
23. Sun-exposed branches were sampled. Listed ERs were standardized to 30°C for samples collected from (a) late May→early August and (b) late August→late September, though stated ranges also reflect standardized ERs obtained using varying values of β. Enclosure temperatures ranged from 5→40°C and PAR varied from 0→≥1400 μmol m^{-2} s^{-1}. Enclosures were set up ∼4 h prior to sampling and inlet air was ozone-scrubbed, May→September, 1, 60–120.
24. Samples were collected at a PPFD of 820 μmol m^{-2} s^{-1} and at leaf temperatures between 25 and 26°C. Leaf temperatures inside the enclosure were stringently monitored and controlled using microthermistors. At constant temperatures and light intensities, variability in emissions for an individual plant ranged from 15 to 30% over a one d period, and within a factor of two over the course of one week. There was a significant diurnal variation, with lower nighttime emissions, even though temperatures at night were within 3°C of daytime temperatures. Enclosure air was scrubbed of oxidants and VOC. Enclosure was tested for surface losses of the analytes; the authors stated that emission rates calculated for most analytes could be up to 20% understated, lab, 11, n.s.
25. ERs listed represent samples collected in spring, early summer, and late summer→autumn, respectively and were normalized to 30°C and PPFD of 1000 μmol m^{-2} s^{-1}. O_3 was removed from inlet air; enclosures were allowed to equilibrate from ∼several h to >1 d before samples were collected, spring→autumn, 2, 22–132.
26. ERs represent ranges detected from 2 control clones (i.e., not exposed to elevated CO_2 or O_3) during June and Aug. (listed as: June range, August range). Enclosure air was scrubbed. Samples were collected at 22–25°C from detached twigs, June, August, 8, 1 (each month).
27. ERs are ranges detected during June and Aug. (listed as: June range, Aug. range, for both ERs and % SQT contribution to total BVOC). Bag temperatures ranged from 16.4–39.9°C. Numerous SQT, non-identified SQT and SQT alcohols were detected. Blank bag testing indicated no detectable release of volatiles, nor were ambient biogenic BVOC observed in inlet air, June, August, 2 (per species), 2–3 (per month).

thwarting future damage from larval feeding (De Moraes et al., 2001). These studies imply that SQT emissions may be significantly enhanced from disturbances such as insect herbivory. Many recent studies have characterized induced BVOC emissions. Several representative reports are described below.

In Black Sage, SQT made up approximately 4% of total BVOC emissions for plants grown in a greenhouse, and <1–70% for plants growing in the field, many of which were infested with aphids (Arey et al., 1995). In late February through April, plants growing in the field emitted a much higher percentage of SQT than plants measured in the greenhouse (from late November to early February). The percentage of SQT (of total BVOC emissions) in field plants was especially high during March and April, when most plants had not yet bloomed and some were heavily infested with aphids. The investigators also noted that field plants emitted significantly less total BVOC and were growing under hotter and more arid conditions than their greenhouse counterparts, possibly leading to smaller available terpene pools in these plants.

Table 3. Contribution of individual SQT chemical species to observed SQT emissions by plant species (in %).

Plant species	aromadendrene	α-bergamotene	β-bisabolene	β-bourbonene	β-Car	α-cadinene	δ-cadinene	γ-cadinene	α-cedrene	β-cedrene	cedrol	β-chamigrene	α-copaene	α-cubebene	β-cubebene	β-cubene	cuparene	α-curcumine
Potato			11–14		38–46													
Thale Cress					∼75							∼5					<2	
Citrus					>98													
Marsh Elder					5–39													
Snapdragon flowers																		
Corn		24–71			1–17													
Loblolly Pine		12			66													
Gray Pine				1							3		1					
Ponderosa Pine					22		6	7						4				
Shortleaf Pine		100																
Beach Pine		77			6		5											
White Pine					7		2		1						4			
Red Pine								1							4			
Loblolly Pine		9–13			26–67			0–2	0–1		0–1							
Rose flowers					22										78			
Scots Pine	0–6			0–5	9–36		7–12	8–23		17–64								
Hornbeam					100													
Norway Spruce			53															
Aleppo Pine	33						26											
Kermes Oak	29						47											
Rock Rose	14			14	14													22
Rosemary	21						28											
Corn		13	2		17													
Siberian Larch																		
Sunflower					∼91													
Silver Birch					10–47								15–46					
European Birch	3–5			0–27	17–25	0–5							0–21			0–7		0–2
Downy Birch	4–6			0–2	46–61	0–2							4–14	0–1		0–6		
Trembling Aspen	2–13			0–1	0–15								0–5	0–1		0–3		18–51
Black Elder				0–3	0–5													5–27

Plant species	β-elemene	7-epi-sesquithujene	α-farnesene	β-farnesene	germacrene-B	germacrene-D	cis-β-guaiene	α-humulene	muurolene	nerolidol	β-selinene	sesquithujene	thujopsene	α-ylangene	α-zingiberene	Reference
Potato			6–10	16–20		13–15										Agelopoulos et al. (2000)
Thale Cress				∼4				∼6					∼8			Chen et al. (2003)
Citrus								<2								Ciccioli et al. (1999)
Marsh Elder						48–54	0–42	5–7								Degenhardt and Lincoln (2006)
Snapdragon flowers										100						Dudareva et al. (2005)
Corn			1–10	0–70						0–4						Gouinguené and Turlings (2002)
Loblolly Pine				11				10								Helmig et al. (2006)
Gray Pine			20	77												Helmig et al. (2007)
Ponderosa Pine				27		10		10	10							Helmig et al. (2007)
Shortleaf Pine																Helmig et al. (2007)
Beach Pine			4	3		5			1							Helmig et al. (2007)
White Pine			57	3				5	13		8					Helmig et al. (2007)
Red Pine			55	41							3					Helmig et al. (2007)
Loblolly Pine	0–1		0–1	8–17	0–1			8–13	0–27	0–6						Helmig et al. (2007)
Rose flowers																Helsper et al. (1998)
Scots Pine									0–7					0–6		Holzke et al. (2006)
Hornbeam																König et al. (1995)
Norway Spruce			25	22												Martin et al. (2003)
Aleppo Pine						22		18								Ormeño et al. (2007b)
Kermes Oak						24										Ormeño et al. (2007b)
Rock Rose						13		1							22	Ormeño et al. (2007b)
Rosemary						25									26	Ormeño et al. (2007b)
Corn		2		37								30				Ruther and Kleier (2005)
Siberian Larch			∼33–83													Ruuskanen et al. (2007)
Sunflower								∼9								Schuh et al. (1997)
Silver Birch			25–75													Vuorinen et al. (2005)
European Birch			5–19						3–49							Zhang et al. (1999)
Downy Birch			0–4					∼7	0–1							Zhang et al. (1999)
Trembling Aspen			10–33					3–36	0–2							Zhang et al. (1999)
Black Elder			33–40													Zhang et al. (1999)

Tomato shoots subjected to caterpillar herbivory emitted elevated levels of SQT (relative to undamaged plants) immediately following insect damage (Maes and Debergh, 2003). Both MT and SQT emissions in the damaged plants exhibited a fluctuating day and nighttime pattern, with peaks observed in both light and dark phases (though nighttime peaks were smaller than those seen during the photoperiod), suggesting that the herbivory occurred both during the day and at night. When the caterpillars were removed from the plants, emissions declined to normal (undamaged) levels within hours. The authors concluded that induced emissions were the result of volatile escape from trichomes ruptured during feeding.

Methyl jasmonate (MeJA) was applied to Norway Spruce saplings to induce chemical defense responses while avoiding physical damage to plant tissues (Martin et al., 2003). The authors observed that induced SQT emissions in saplings followed a diurnal time course, peaking during light periods. SQT emissions increased by a factor of 30, and became more dominant in the mixture of volatiles emitted. Maximum emissions occurred during the photoperiod 1–2 days after treatment, and then slowly declined. The authors noted that terpenes were largely absent from needle oleoresin, and were the dominant products of terpene synthase activity observed post-treatment. These observations led to the conclusion that the induced volatiles appeared to have been synthesized de novo following MeJA treatment, in lieu of being released from storage pools.

The emissions and molecular regulation of volatiles released by forest tent caterpillar (FTC)-infested poplar leaves and non-infested systemic leaves (from infested trees) were examined by Arimura et al. (2004). Both infested and systemic leaves released similar blends of volatiles, including SQT, though directly infested leaves released higher overall amounts. FTC-induced volatile emissions were low on the first day after FTC feeding, but became significant within 24-h, lasting for ∼3 days during feeding. After removal of FTC, emissions of germacrene-D continued for 24 h before declining. FTC-infested leaves emitted higher amounts of germacrene-D than mechanically-wounded leaves. Unwounded control trees did not produce detectable amounts of analytes. The amount of germacrene-D released from FTC-infested trees was variable, possibly due to tree-to-tree variations and/or FTC feeding behavior variations. Emissions of other induced volatiles followed a pattern similar to that of germacrene-D. Based on the isolation and study of a germacrene-D synthase during this investigation, the authors concluded that transient and diurnal volatile emissions are at least partly regulated by the level of transcription of this synthase.

In the 1999 Ciccioli et al. study, investigators noted that some of the Navel orange trees sampled for emissions were infected with the *Citrus* quick decline virus, but these trees did not show significantly different emission rates than healthy trees. This is an interesting finding, suggesting the possibility that emissions might only be induced by infestations that are potentially alleviated through chemical signaling of herbivore predators, and not necessarily by diseases such as viral infections.

2.2.4 Variability among individuals

The emissions from individuals within a species can vary considerably, even when other environmental variables are constant. For sunflower, Schuh et al. (1997) observed variability in SQT emission rates on the order of a factor of ∼3–4 between individual plants, even though all individuals were at the same vegetative stage and light/temperature regimes were identical. A similar phenomenon was observed in Scots Pine, with near-simultaneous measurements from 2 trees revealing differences (in total SQT ERs) from a few percent to ∼one order of magnitude depending on the month considered (Holzke et al., 2006). Additionally, the contributions of individual SQT chemical species to total SQT emissions varied considerably between individual Scots Pine trees. Significant intraspecific variability has also been reported for Downy Birch (Hakola et al., 2001) and potato (Agelopoulos et al., 2000). Not surprisingly, variability of up to one order of magnitude has been observed across different cultivated varieties of *Citrus* (Ciccioli et al., 1999) as well as between ecotypes of *Arabidopsis thaliana* (Tholl et al., 2005). Though the reasons for such substantial variability between individuals are not well understood, numerous factors may be at work, such as prior herbivore feeding, which can possibly trigger permanent biochemical changes in terpenoid pathways and rates of terpene synthase gene expression (Huber et al., 2004). In any case, this significant source of variation in ERs should be kept in mind when applying results from emissions experiments.

3 Sesquiterpene emitting plant species, quantities of emissions, and chemical species identifications

3.1 Sesquiterpene emission rates

Table 2 outlines 27 studies that report biogenic SQT emissions. Also presented are the plant species studied, the quantities and chemical species of SQT emitted, and (where available) the percent contributions of those compounds to total BVOC emissions for each plant species. For each study there is a brief assessment of whether or not the emissions data are quantitative. This determination was made based on several factors, such as whether or not the emissions were normalized to plant biomass, whether or not there was substantial uncertainty regarding quantification of emissions (as determined by the authors of each published study), etc. Also included for each study is a footnote containing ancillary information (i.e., sampling dates, number of specimens measured, etc.) that may be of use to the reader. Our efforts to present reported emissions data in a standardized fashion were limited in some cases, as discussed below.

Many, but not all, of the studies summarized in Table 2 report emission rates normalized to a standard temperature. Additional information regarding temperature data and other information associated with reported ERs is provided in the Table 2 footnotes. Some investigators have reported SQT ERs normalized to plant biomass, while others have not. These ERs have been separated into appropriate columns. While most investigators who normalized emissions to plant biomass used dry weight as a metric, a few reported volatiles released per quantity of fresh weight. The ERs in Table 2 that fall into this latter category have been marked with asterisks, and suggested dry to fresh weight conversions are given following Table 2, for both coniferous and broadleaf tree species. These suggested conversions are based on personal observations made by the authors (unpublished data). Still other studies reported ERs per m^2 leaf area, and the reader will find these listed in a separate column.

From an inspection of Table 2 it is obvious that there exists substantial variability in emissions between and within plant species, with ER values observed from <10 to $78\,000\,\mathrm{ng\,g_{DW}^{-1}\,h^{-1}}$. The percent contribution of SQT to total observed BVOC also varies considerably, ranging from <1 to 100% of the total BVOC ER. When one considers only the emissions data from Table 2 that were reported as emissions per gram (fresh or dry weight) of plant matter per hour, the average SQT ER across all species is $\sim 3000\,\mathrm{ng\,g_{DW}^{-1}\,h^{-1}}$. It is important to recognize that these values may not reflect average "real-world" emissions. Numerous ERs reported in Table 2 are based on single measurements (using one plant specimen), and many of the early SQT enclosure studies did not carefully control enclosure temperatures and other important experimental parameters, such as disturbances to the enclosed specimens during enclosure set-up. These studies may have reported artificially-enhanced SQT emissions, while other studies may have neglected some of the analytical steps necessary to quantitatively measure SQT, thereby possibly underestimating SQT fluxes. It should also be noted that the vegetation species chosen in these experiments most likely do not represent a random selection, but instead are frequently-sampled SQT-emitting species chosen because of researcher interest in studying SQT emissions. Therefore, these values should not be considered as "average" emissions from all terrestrial vegetation. We attempted to calculate average SQT ERs as a function of plant functional type (PFT) using all available data (with the exception of published ERs which exceeded $50\,000\,\mathrm{ng\,g_{DW}^{-1}\,h^{-1}}$, as these were possibly elevated due to disturbance-induced emissions bursts). When normalized to 30°C, average values (presented with corresponding standard deviations) for coniferous trees, broadleaf trees, shrubs, and crops are 290 ± 410, 1410 ± 2200, 7060 ± 6830 and $190\pm430\,\mathrm{ng\,g_{DW}^{-1}\,h^{-1}}$, respectively. Given the paucity of available data and the high standard deviations of PFT-specific ERs, SQT emissions currently cannot be accurately characterized according to plant growth forms.

3.2 Relative abundances of reported sesquiterpene compounds

It is important to consider and evaluate which SQT chemical species are the important players in biogenic emissions, as individual compounds have significantly different reactivities, and thus different atmospheric fates.

In order to determine which biogenically-emitted SQT have been observed to dominate individual SQT emission profiles, we examined the relative contribution of individual SQT chemical species to total observed SQT emissions for different plant species, based on studies that have speciated these compounds. Table 3 contains a list of individual SQT and their relative contribution to overall SQT emissions from these studies. As disturbance is known to affect the quality of SQT blends emitted, investigations that reported disturbance-induced SQT emissions were excluded from Table 3. Unidentified SQT chemical species were also excluded, although numerous investigators have reported ERs for these compounds. β-Car is the most frequently reported SQT, and is also one of the most abundant SQT chemical species within many SQT emissions profiles. α- and β-farnesene are also prominent contributors to observed SQT profiles, as is α-humulene. Though less frequently reported, aromadendrene, α-bergamotene, δ-cadinene, and germacrene-D have all been observed to contribute significantly to biogenic SQT emissions in some species.

4 Conclusions

The task of synthesizing the various published SQT emissions studies is greatly complicated by a lack of standardized reporting practices. This reality creates a major difficulty for modelers of biogenic SQT processes, who seek to increase both vegetation and chemical species information included in current biogenic emissions inventories. Some authors normalize SQT emissions to dry vegetation weight, while others use fresh weight. Many authors standardize their emission factors according to previously-existing algorithms, while others report values which represent emissions across a range of temperatures. And while most authors report light intensity in terms of PPFD ($\mu\mathrm{mol\,m^{-2}\,s^{-1}}$), some report this parameter as illuminance (e.g., $\mathrm{lm\,m^{-2}\,s^{-1}}$), which is a poorly-suited measure of light intensity within the context of plant science. One particularly useful improvement to reporting practices is to include the values of empirical parameters used to calculate standardized emission rates, such as β-factors and other coefficients. Additionally, specific temperatures and PPFDs measured during sample acquisition periods should be made available, rather than ranges of values observed over multiple sample collection periods. Finally, when standardizing emissions to biomass, it would be sensible to report emissions as a function of dry vegetation weight,

in lieu of using fresh weight as a metric, since leaf water content can vary significantly even within a single specimen.

β-Car, α- and β-farnesene, and α-humulene are the most commonly reported biogenically-emitted SQT chemical species, though aromadendrene, α-bergamotene, δ-cadinene, and germacrene-D have also been identified as significant compounds in some plant species. SQT emissions typically increase with temperature. The effects of light and stomatal control on SQT emissions are less clear. Significant seasonal variation observed in the contribution of SQT to total BVOC emissions creates the possibility that SQT and their roles in atmospheric processes are especially prominent during warmer times of the year, particularly in late spring to mid-summer. Further characterization of seasonally-dependant SQT emissions is needed. Another source of substantial uncertainty is the variability in SQT emissions among individuals within a species, and (to an even greater extent) between different species. Though the enclosure studies clearly show that disturbances to vegetation are important in controlling short-term SQT emissions bursts, the time-averaged magnitude of disturbance-induced emissions (from herbivores and severe weather events) under ambient conditions is highly uncertain, and additional studies of disturbance as a driver of SQT emissions are needed.

Based on the biogenic SQT emissions studies reviewed here, SQT emission rates cover a wide range of values, varying between individuals and across species, as well as at different temperatures and phenological states. These published emission rates range from <10 to $>10\,000\,\mathrm{ng\,g_{DW}^{-1}\,h^{-1}}$, but this range is heavily influenced by early SQT studies, which may have reported artificially-elevated SQT emission rates due to higher-than-ambient enclosure temperatures and disturbances to enclosed vegetation prior to and during sample collection. Furthermore, vegetation species that were chosen for these experiments probably do not represent a random selection, but instead are species that were selected because of researcher interest in studying SQT emissions. Therefore, averages that are computed based on published data probably result in higher SQT emissions than what is actually emitted from the biosphere. These observations make the characterization of landscape and global SQT fluxes highly uncertain, and underscore the need for screening of numerous species as well as the collection of multiple replicates from several individuals within a given species. It is still unclear whether SQT emissions may be adequately modeled as a function of plant functional type (e.g. broadleaf trees, herbs, etc.) or according to some other grouping scheme. An appropriate approach for quantifying global distributions of SQT emissions remains to be elucidated.

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