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Biogenic volatile organic compound emissions from nine tree species used in an urban tree-planting program

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HIGHLIGHTS

- MT and SQT ERs were determined from nine tree species in an urban planting program.
- The chosen tree species behaved as low emitters in the Colorado urban environment.
- Emission scenarios for low-emitting species were compared to high-emitting species.
- Model findings showed marked emission savings from planting low-emitting species.

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ABSTRACT

The biogenic volatile organic compound (BVOC) emissions of nine urban tree species were studied to assess the air quality impacts from planting a large quantity of these trees in the City and County of Denver, Colorado, through the Mile High Million tree-planting initiative. The deciduous tree species studied were Sugar maple, Ohio buckeye, northern hackberry, Turkish hazelnut, London planetree, American basswood, Littleleaf linden, Valley Forge elm, and Japanese zelkova. These tree species were selected using the i-Tree Species Selector (itreetools.org). BVOC emissions from the selected tree species were investigated to evaluate the Species Selector data under the Colorado climate and environmental growing conditions. Individual tree species were subjected to branch enclosure experiments in which foliar emissions of BVOC were collected onto solid adsorbent cartridges. The cartridge samples were analyzed for monoterpenes (MT), sesquiterpenes (SQT), and other C_{10}–C_{15} BVOC using thermal desorption-gas chromatography–flame ionization detection/mass spectroscopy (GC–FID/MS). Individual compounds and their emission rates (ER) were identified. MT were observed in all tree species, exhibiting the following total MT basal emission rates (BER; with a 1–σ lower bound, upper bound uncertainty window): Sugar maple, 0.07 (0.02, 0.11) μg g^{-1} h^{-1}; London planetree, 0.15 (0.02, 0.27) μg g^{-1} h^{-1}; northern hackberry, 0.33 (0.09, 0.57) μg g^{-1} h^{-1}; Japanese zelkova, 0.42 (0.26, 0.58) μg g^{-1} h^{-1}; Littleleaf linden, 0.71 (0.33, 1.09) μg g^{-1} h^{-1}; Valley Forge elm, 0.96 (0.01, 1.92) μg g^{-1} h^{-1}; Turkish hazelnut, 1.30 (0.32, 2.23) μg g^{-1} h^{-1}; American basswood, 1.50 (0.40, 2.70) μg g^{-1} h^{-1}; and Ohio buckeye, 6.61 (1.76, 11.47) μg g^{-1} h^{-1}. SQT emissions were seen in five tree species with total SQT BER of: London planetree, 0.11 (0.01, 0.20) μg g^{-1} h^{-1}; Japanese zelkova, 0.11 (0.05, 0.16) μg g^{-1} h^{-1}; Littleleaf linden, 0.13 (0.06, 0.21) μg g^{-1} h^{-1}; northern hackberry, 0.20 (0.11, 0.30) μg g^{-1} h^{-1}; and Ohio buckeye, 0.44 (0.06, 0.83) μg g^{-1} h^{-1}. The following trees exhibited emissions of other C_{10}–C_{15} volatile organic compounds (VOC): Littleleaf linden, 0.15 (0.10, 0.20) μg g^{-1} h^{-1}; Ohio buckeye, 0.39 (0.14, 0.65) μg g^{-1} h^{-1}; and Turkish hazelnut, 0.72 (0.49, 0.95) μg g^{-1} h^{-1}. All tree species studied in this experiment were confirmed to be low isoprene emitters. Compared to many other potential urban tree species, the selected trees can be considered low to moderate BVOC emitters under Colorado growing conditions, with total emission rates one-tenth to one-hundredth the rates of potential high-BVOC emitting trees. The emissions data were used to estimate the impact of this targeted tree planting on the urban BVOC flux and atmospheric VOC burden. Selecting the low-emitting tree species over known high BVOC emitters is equivalent to avoiding VOC emissions from nearly 500,000 cars from the inner city traffic.

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1. Introduction

Many cities have adopted large-scale tree-planting initiatives to increase tree cover in an effort to sequester carbon, reduce the urban heat island effect, conserve energy for heating and cooling buildings, and beautify neighborhoods (McPherson et al., 2011; Morani et al., 2011). Urban tree planting is also a cost-effective means to improve air quality.

Many trees release significant amounts of biogenic volatile organic compounds (BVOC) into the atmosphere, including isoprene, monoterpenes (MT) and sesquiterpenes (SQT). The photochemical reaction of these compounds can contribute to the formation of ozone and secondary organic aerosol (Fehsenfeld et al., 1992; Finlayson-Pitts and Pitts, 2000; Hewitt, 1999; Ryerson et al., 2001). BVOC emissions can vary widely among tree species and even within species depending on physiological and environmental factors (Benjamin and Winer, 1998). Calfapietra et al. (2013) recently reviewed the current literature concerning BVOC and urban environments. Their assessment of existing research underlines the role tree selection plays when considering the potential for BVOC emissions.

One of the earliest studies to recognize the importance of selecting low volatile organic compound (VOC)-emitting tree species for large-scale tree-planting programs was performed by Benjamin et al. (1996). Some common tree species such as oak and pine emit large quantities of BVOC into the atmosphere; consequently, planting such tree species in large numbers could potentially worsen inner city air quality. These researchers developed a methodology based on taxonomic relationships to assign emission rates to trees in Southern California and ranked over 300 tree species on a scale of low-emitting to high-emitting species. The scale defined species emitting 0.01–1 μg g dw^{-1} h^{-1} VOC as low emitters, 1–10 μg g dw^{-1} h^{-1} as moderate emitters, and 10–1000 μg g dw^{-1} h^{-1} as high emitters.

A mesoscale meteorological and photochemical modeling study performed by Taha (1996) for the California South Coast Air Basin showed that increased tree-planting would result in a net decrease in ozone as long as the trees were low hydrocarbon emitters. These authors determined that tree species that emitted more than 2 μg g^{-1} h^{-1} isoprene and 1 μg g^{-1} h^{-1} MT (based on episode-specific simulations) would worsen ozone levels under urban ambient air conditions.

Donovan et al. (2005) used an atmospheric chemistry model to develop an urban tree air quality score (UTAQS) to rank trees in the Birmingham area of the United Kingdom in order of their potential to improve air quality (high, medium and low). A score was assigned based on the trees' BVOC emissions and capacity for pollutant deposition onto vegetative surfaces. The study's authors noted that tree planters anywhere could utilize the classification system with the appropriate input data for a particular location.

An alternative approach to ranking trees was developed for a tree-planting project in Sacramento, California, called the Tree BVOC Index (Simpson and McPherson, 2011). The authors presented a method to calculate BVOC emissions from urban trees that can be used by tree-planting programs seeking to transition to lower BVOC emitters in future plantings.

Several studies have investigated the benefits and costs of large-scale urban tree-planting programs with respect to such factors as energy savings and air quality improvements (McPherson et al., 1998, 2005; Soares et al., 2011). A recent review of urban tree literature by Roy et al. (2012) discusses tree benefits, costs, and assessment methods. In all the studies, limitations considered, benefits outweighed costs.

The City and County of Denver in Colorado have implemented a program, called the Mile High Million (milehighmillion.org) with the goal to plant a million trees within the Denver metropolitan region by 2025. The tree species selected for the Mile High Million were chosen based on their suitability for planting in Denver's urban environment, i.e. they have a history of successful growth in this climate, soil, moisture levels, wind and snow loads, their ability to remove air pollutants, and their standing as low emitters of BVOC. The tree species in this study were selected using the i-Tree Species Selector (itreetools.org), with the choice of these species based on a variety of criteria. These include their ability to provide building energy use reduction through shading, their ability to remove air pollutants, and be low BVOC emitters themselves, with the objective to limit introducing VOC sources into the inner city environment and their contribution to pollution formation, i.e. ozone and organic aerosols. While tree species in the present study were specifically selected for being low-emitting species using literature information, an objective in this work was to validate that the selected trees would behave as such under Colorado and inner city growing conditions. In addition, we were interested in determining what effect these tree species would have on the urban BVOC flux and atmospheric VOC burden if scaled up to simulate an urban tree planting initiative. For comparison, we also wanted to perform the same simulation on known high BVOC emitting species.

2. Experimental methods

2.1. Site description

The experiments were conducted from June 2 to October 8, 2010, at the Creekside Tree Nursery in Boulder, Colorado, USA, approximately 30 km NW of Denver. An enclosed trailer at the tree nursery was utilized as a mobile field laboratory. Trees were provided by the nursery and the City and County of Denver. Nine tree species were studied: sugar maple (*Acer saccharum* Marshall), Ohio buckeye (*Aesculus glabra* Willd.), northern hackberry (*Celtis occidentalis* L.), Turkish hazelnut (*Corylus colurna* L.), London planetree (*Platanus* × *acerifolia* Aiton Willd.), American basswood (*Tilia americana* L.), littleleaf linden (*Tilia cordata* Mill.), Valley Forge elm (*Ulmus americana* L. 'Valley Forge'), and Japanese zelkova (*Zelkova serrata* Thunb. Makino). All trees were between two and three meters tall and between three and five years old. The trees were watered daily and received full exposure to sunlight. No fertilizer was applied during the studies. Trees remained in their planting pots during the experiments.

2.2. Tree selection

Tree species were selected using the i-Tree Species Selector software from the USDA Forest Service (available at http://www.itreetools.org/species/index.php). An example of the input screen is shown in the Supplemental Materials. A value of 10 on the importance scale (where 0 represents the least important and 10 the most important) was input in the Air Pollutant Removal category for the following compounds: carbon monoxide, ozone, nitrogen dioxide, sulfur dioxide, and particulate matter. A value of 10 on the importance scale was also input in the categories of low VOC emissions and building energy reduction. Based on the report generated, selection was narrowed to deciduous trees with a track record of performing well in Denver's climate, soil, moisture levels, wind loads, and snow loads. These species were compared against the Denver street tree list and what was readily available from the City and County of Denver's vendors.

2.3. Sampling

Sampling methods and materials used for the BVOC emission measurements followed the procedures of Ortega et al. (2008) and Baghi et al. (2012). Sampling conditions were identical to those in Baghi et al. (2012) and are briefly outlined below, noting any variations. A branch of the studied vegetation was enclosed in a ~50 l volume Tedlar bag with minimal contact of foliage with the bag. Ambient air was filtered for particles (respirator filter) and scrubbed of ozone (cartridge with MnO_2-coated screens) and pumped at 25 l min^{-1} into the enclosure providing a slight overpressure inside the bag. A small flow of a 5-component VOC reference standard mixture, spanning a wide volatility range was doped into the purge air to serve as a reference for tracing compound recovery rates from the experiment (Ortega and Helmig, 2008).

Two automated sampling devices (Helmig et al., 2004) were used for collection of emission samples, allowing for 10–20 samples to be collected sequentially. Samples were collected onto 9 cm long × 0.64 cm o.d. glass tubes filled with a multi-adsorbent bed composed of 0.10 g Tenax GR and 0.31 g Carboxen 1016 (Supelco, Bellefonte, PA, USA). A second adsorbent cartridge (to test for breakthrough) was placed in series with every 10th sample cartridge. Sampling flow was 200 ml min^{-1} over 1 h for a typical sample volume of 12 l. Cartridges were maintained at 40 °C to minimize co-collection of water onto the tubes (Karbiwnyk et al., 2002).

For each tree, a single branch was chosen for sampling. After careful installation to minimize any disturbance effects, the branch enclosure, while being purged, was allowed to equilibrate for at least 6 h before sampling. Sampling times varied from 1 h during daytime to 2 h during nighttime. 249 sample results were obtained over the course of this study, from June to September 2010: 15 samples for sugar maple, 20 samples for Ohio buckeye, 15 samples for northern hackberry, 18 samples for Turkish hazelnut, 32 samples for London planetree, 16 samples for American basswood, 58 samples for littleleaf linden, 36 samples for Valley Forge elm, and 39 samples for Japanese zelkova (Table 1). In addition, 20 samples of the inlet purge air were collected to allow for a comparison of the aromatic reference standard recovery rates from the experiment.

Samples collected at the field site were brought back to the laboratory for analysis. After thermal desorption using a Perkin–Elmer ATD 400 instrument, volatilized VOC were transferred onto a gas chromatograph (GC, Model 5890, Hewlett–Packard). Separation was achieved on a 0.32 mm i.d., 50 m long, 5 μm film thickness DB-1 capillary column (Agilent). Analyte identification and quantification were performed using a mass spectrometer (MS, Model 5970, Hewlett–Packard) and a flame ionization detector (FID), respectively, after splitting the column flow. Similar instrumentation and calibration procedures have been described previously (Helmig et al., 2004; Ortega et al., 2008). Compound identification was achieved using relative retention times, along with comparing mass spectra with the NIST database. Due to the lack of standards and uncertainties in the GC retention indices, some of the SQT speciations should be considered as tentative only. All quantifications were performed using the FID signal. FID response factors were established by sampling and analyzing quantitative gas-phase VOC standards in a similar fashion as the field samples. Quantitative results are reported in mass of compound.

2.4. Biomass dry weight determination

The dry biomass weight of the enclosed plant material was determined to normalize emission rates. For all trees studied, leaves were harvested from sampled branches after the experiment. Collected biomass was dried for ≥24 h in a 50 °C oven.

2.5. Environmental monitoring

Environmental variables monitored were ambient air temperature, air temperature inside the enclosure, leaf temperature, relative humidity inside the enclosure, photosynthetically-active radiation (PAR; measured outside the enclosure next to the bag using an SB 190 quantum sensor, LI-COR, Lincoln, NE, which measures PAR in the 400–700 nm waveband), and ozone using the same equipment as described in Ortega et al. (2008) and Baghi et al. (2012). Environmental data were acquired at 1 s intervals and averaged and recorded every 5 min using a Campbell Scientific CR10X datalogger (Campbell Scientific, Logan, UT, USA).

2.6. Normalized emission rate calculations

Temperature dependencies for emissions of MT and SQT were observed in this study. Light dependency was seen for isoprene emission. Normalized emission rates, here referred to as basal emission rates (BER), were calculated for conditions of $T_s = 30$ °C using the algorithm of Guenther et al. (1993), $E = \mathrm{BER}[\exp \beta(T - T_s)]$, where E is emission rate, T is leaf temperature, and β is the beta-factor calculated from the experimental results of each tree. For each BVOC class for each tree species, measured emission rates were plotted against T. BER were obtained for $T = 30$ °C from a best exponential fit to the data. In cases where data did not show a good fit to an exponential curve (R^2 values < 0.50), BER were determined as the median of all data after normalizing each data point to 30 °C using β-values of 0.10 °C^{-1}, 0.17 °C^{-1}, and 0.10 °C^{-1} for MT, SQT, and other VOC, respectively (Ortega et al., 2008). The leaf dry weight determinations were used to normalize the emission rates to the amount of biomass inside the enclosure. ER results are reported in μg compound g^{-1} h^{-1}.

BER values are reported with lower bound and upper bound values based on a 1−σ uncertainty of the exponential fit. Uncertainty was calculated using the fit and predint functions on MATLAB (MathWorks) using the least-squares experimental fitting tool and deriving from that the 1−σ uncertainty window for $T = 30$ °C (see Supplement Fig. 2 for an example). For cases where the regression fit was poor, the lower and upper bound values were determined using the standard deviation of all data after normalizing each data point to 30 °C using the β-values given above. This uncertainty is a variable that reflects the data distribution, and the robustness of the fit of the exponential regression through the data. This uncertainty does not consider errors in the experimental variables, such as those from flow rates of enclosures, sampling rates, and uncertainty in the FID response factor and GC quantification. In our experience, those variables typically have relative errors on the order of 2–5% each, resulting in a combined maximum uncertainty of ~20% (using error propagation from these variables). Consequently, the regression analysis in most cases is the largest contributing factor. The total uncertainty window was determined for each plant species by adding the respective regression fit uncertainty to the estimated 20% experimental error margin.

2.7. Modeling

Denver is located at the foot of the Rocky Mountains in a high plains region at an elevation of ~1600 m above sea level. It has a semi-arid continental climate with four distinct seasons. The urban

Table 1
Total isoprene, monoterpene, sesquiterpene, and other VOC basal emission rates (BER) and temperature coefficients for observed temperature dependencies.

Common name	No. of enclosures	Total no. of samples	Enclosure temperature range (°C)	Dates sampled (year 2010)		
Sugar maple	1	15	9–35	Sept 19–20		
Ohio buckeye	1	20	11–39	Jun 23–24		
Northern hackberry	1	15	9–24	Sept 21–22		
Turkish hazelnut	1	18	14–32	Jul 2–3		
London planetree	1	32	12–32	Aug 6–7, Oct 7–8		
American basswood	1	16	10–32	Jun 21–22		
Littleleaf linden	2	58	8–32	Jun 2–3, Aug 4–5, Aug 30–31		
Valley Forge elm	2	36	8–36	Jun 30–Jul 1, Sept 9–10		
Japanese zelkova	2	39	11–31	Jun 3–4, Jul 23–24		
	Total BER ($\mu g\ g^{-1}\ h^{-1}$)					
	Isoprene[a]	β (isoprene) ($°C^{-1}$)	R^2 (isoprene)	MT	β (MT) ($°C^{-1}$)	R^2 (MT)
Sugar maple	<0.01	n/a	n/a	0.07 (0.02, 0.11)[b]	–	–
Ohio buckeye	<0.01	n/a	n/a	6.61 (1.76, 11.47)	0.14	0.64
Northern hackberry	<0.01	n/a	n/a	0.33 (0.09, 0.57)[b]	–	–
Turkish hazelnut	<0.01	n/a	n/a	1.30 (0.32, 2.23)[b]	–	–
London planetree	0.14 (0.01, 0.29)	0.31	0.81	0.15 (0.02, 0.27)[b]	–	–
American basswood	<0.01	n/a	n/a	1.50 (0.40, 2.70)[b]	–	–
Littleleaf linden	<0.01	n/a	n/a	0.71 (0.33, 1.09)[b]	–	–
Valley Forge elm	<0.01	n/a	n/a	0.96 (0.01, 1.92)	0.20	0.58
Japanese zelkova	<0.01	n/a	n/a	0.42 (0.26, 0.58)[b]	–	–
	Total BER ($\mu g\ g^{-1}\ h^{-1}$)					
	SQT	β (SQT) ($°C^{-1}$)	R^2 (SQT)	Other VOC	β (other VOC) ($°C^{-1}$)	R^2 (other VOC)
Sugar maple	<0.01	n/a	n/a	<0.01	n/a	n/a
Ohio buckeye	0.44 (0.06, 0.83)	0.19	0.85	0.39 (0.14, 0.65)	0.11	0.75
Northern hackberry	0.20 (0.11, 0.30)[c]	–	–	<0.01	n/a	n/a
Turkish hazelnut	<0.01	n/a	n/a	0.72 (0.49, 0.95)[d]	–	–
London planetree	0.11 (0.01, 0.20)[c]	–	–	<0.01	n/a	n/a
American basswood	<0.01	n/a	n/a	<0.01	n/a	n/a
Littleleaf linden	0.13 (0.06, 0.21)	0.05	0.51	0.15 (0.10, 0.20)[d]	–	–
Valley Forge elm	<0.01	n/a	n/a	<0.01	n/a	n/a
Japanese zelkova	0.11 (0.05, 0.16)[c]	–	–	<0.01	n/a	n/a

[a] For light-dependent compounds, the ERs were corrected for light prior to fitting exponentially using $C_{PAR} = 1000[(1 + (0.0027*PAR)^2)^{1/2}/(2.878*PAR)]$, where C_{PAR} is the light-correction factor.
[b] For these MT BER, the data were not fitted to an exponential curve, rather they are reported as the median (with lower bound, upper bound 1–σ uncertainty window in parentheses) after normalizing each sample to 30 °C using a β of 0.10 $°C^{-1}$.
[c] For these SQT BER, the data were not fitted to an exponential curve, rather they are reported as the median (with lower bound, upper bound 1–σ uncertainty window in parentheses) after normalizing each sample to 30 °C using a β of 0.17 $°C^{-1}$.
[d] For these Other VOC BER, the data were not fitted to an exponential curve, rather they are reported as the median (with lower bound, upper bound 1–σ uncertainty window in parentheses) after normalizing each sample to 30 °C using a β of 0.10 $°C^{-1}$.

forest covers 19.7% of the 397 km^2 land area that comprises the City and County of Denver (Denver Parks and Recreation Forestry Division, 2013).

BVOC emissions for Denver, Colorado, were estimated using the Model of Emissions of Gases and Aerosols from Nature (MEGAN) as described in Guenther et al. (2006). Emissions were treated as $E = E_0[\exp \beta(T - T_s)]$. E_0 was obtained by converting our experimentally determined BER ($\mu g\ g^{-1}\ h^{-1}$) into an aerial flux estimate using plant functional type (PFT) per unit leaf areas ($g\ m^{-2}$). A PFT-specific average of specific leaf weight (SLW) of 100 $g\ m^{-2}$ was used for deciduous broadleaf temperate trees (Guenther et al., 1995; Lathiere et al., 2006). β-values of 0.10, 0.17, and 0.13 $°C^{-1}$ were used for MT, SQT, and isoprene, respectively (Guenther et al., 2012; Ortega et al., 2008). Isoprene, MT, and SQT emissions were calculated for the period May 1–October 15. Historical hourly temperature inputs from 2010 for Denver were obtained from Weather Underground (2013). For isoprene, ER were corrected for light-dependence by applying $C_{PAR} = 1000[(1 + (0.0027*PAR)^2)^{1/2}/(2.878*PAR)]$, where C_{PAR} is the light correction factor (Guenther et al., 1991). Historical average hourly photosynthetically active radiation (PAR) data from 2010 for Nunn, CO were obtained from the USDA UV-B Monitoring and Research Program website (Natural Resource Ecology Laboratory, 2013). Observed emission rates from the experimental results of this study were included in the model to simulate BVOC emissions from an urban tree canopy and consisted of the trees investigated in this study. For a comparison, isoprene, MT, and SQT emission rates from high-BVOC-emitting oak species, Kermes oak, *Quercus coccifera* L. (Karl et al., 2009; Staudt and Lhoutellier, 2011) and English oak, *Quercus robur* L. (Karl et al., 2009) (isoprene only) were input into the model, as well. Tree cover data were obtained from the City and County of Denver Forestry Division's website (Denver Parks and Recreation Forestry Division, 2013). According to the Denver Forestry Division, Denver's urban forest contains 2.2 million trees, which cover 78 km^2 of the 397 km^2 region. One million trees would cover approximately 36 km^2, or 9% of the 397 km^2 region. A leaf area index (LAI) of 4 (leaf m^2 ground m^{-2}) was used in the calculations for the Denver region (McPherson et al., 2013).

3. Results and discussion

3.1. Chemical identification

The MT, SQT, and other C_{10}–C_{15} VOC identified by GC–FID/MS in the emission studies of each tree species are listed in Table 2. The table does not include isoprene emissions, which were detected in one tree species, London planetree. All tree species were found to emit MT, and sixteen MT were identified all together. A total of five SQT were observed from five tree species. Our methods identified six other VOC emissions in three tree species.

Table 2
VOC identified via GC–FID/MS from each of the tree species.

	Sugar maple	Ohio buckeye	Northern hackberry	Turkish hazelnut	London planetree	American basswood	Littleleaf linden	Valley Forge elm	Japanese zelkova
Monoterpenes	α-Pinene Limonene *Trans*-ocimene	α-Pinene Limonene *Trans*-ocimene Tricyclene Camphene Sabinene β-Pinene Myrcene α-Terpinene Terpinolene	Limonene *o*-Cymene	α-Pinene Limonene *Trans*-ocimene β-Pinene 3-Carene	Limonene α-Thujene	α-Pinene Limonene Myrcene *Cis*-ocimene	Limonene Camphene α-Thujene	α-Pinene Limonene β-Pinene Terpinolene α-Thujene γ-Terpinene Ocimene	α-Pinene Limonene
Sesquiterpenes		Caryophyllene α-Guaiene α-*Trans*-bergamotene	α-Himachalene		β-Gurjunene		α-Himachalene		β-Gurjunene
Other VOC		Sabinene hydrate Terpineol-4 α-Terpineol		Nonanal *Trans*-verbenol		α-Ionone			

3.2. Emission rate results

The BER for the BVOC measured from the nine tree species studied are shown in Table 1. Detailed results for each of the species investigated are provided in the following section.

3.2.1. Sugar maple (A. saccharum Marshall)

Three MT emissions were observed: α-pinene, limonene, and *trans*-ocimene. Fig. 1 shows emission rate results for a typical day for each compound. Limonene and *trans*-ocimene comprised 47% and 43% of the total MT emissions, respectively, and α-pinene held 10% of the total emissions. The total normalized MT emission rate was 0.07 (lower bound 0.02, upper bound 0.11 1−σ uncertainty window) μg g^{-1} h^{-1}. The total MT emission rate observed in this study falls within the values reported in Ortega et al. (2008) for Sugar maple and for other *Acer* species reported by Benjamin et al. (1996), Kesselmeier and Staudt (1999), and Nowak et al. (2002).

3.2.2. Ohio buckeye (A. glabra Willd.)

Ohio buckeye exhibited the largest number of MT, SQT, and other VOC emissions of the species investigated in this study. This tree species also exhibited the largest total MT and SQT basal emission rates. Tricyclene, α-pinene, camphene, sabinene, β-pinene, myrcene, α-terpinene, limonene, *trans*-ocimene, and terpinolene were the observed MT. The SQT seen included caryophyllene, α-*trans*-bergamotene, and α-guaiene. In addition to MT and SQT, sabinene hydrate, 4-terpineol, and α-terpineol were other C_{10} VOC identified in Ohio buckeye. All observed compounds emitted from Ohio buckeye exhibited strong temperature dependence. As an example, the total SQT emission rate temperature dependence is shown in Fig. 2. Table 3 shows the speciation of the compounds in the emission samples as a percent of each compound of the total MT and SQT emissions. Of the other VOC, sabinene hydrate comprised 71%, 4-terpineol 10%, and α-terpineol 19%. The total MT BER for Ohio buckeye was 6.61 (1.76, 11.47) μg g^{-1} h^{-1}. The SQT BER was determined to be 0.44 (0.25, 0.52) μg g^{-1} h^{-1}, and the other VOC BER was 0.39 (0.14, 0.65) μg g^{-1} h^{-1}. The MT BER determined here is higher than what has been previously estimated by Nowak et al. (1.6 μg C g^{-1} h^{-1}) (2002), but on the same order of magnitude. Kesselmeier and Staudt (1999), who compiled normalized emission rates of numerous tree species, reported other *Aesculus* spp. to emit <0.2 μg g^{-1} h^{-1} MT (see Table 4).

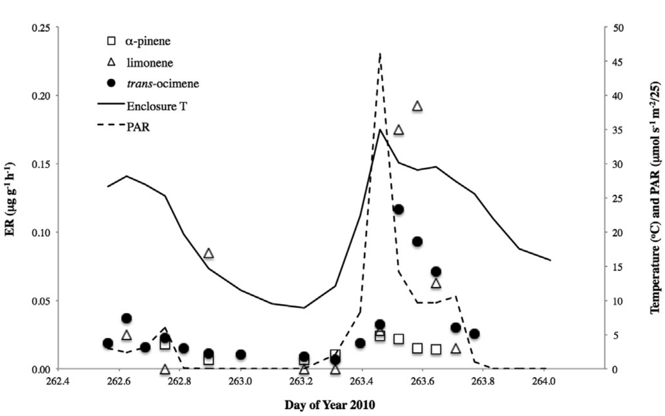

Fig. 1. Profile of monoterpene (MT) emission rate (ER) based on individual hourly measurements from a Sugar maple tree (*Acer saccharum* Marshall) over a two day sampling period (September 19–20, 2010) with concurrent enclosure temperature (°C) and photosynthetically active radiation (PAR, μmol s^{-1} m^{-2}). The PAR scale was reduced by a factor of 25 to allow display on the same axis as temperature.

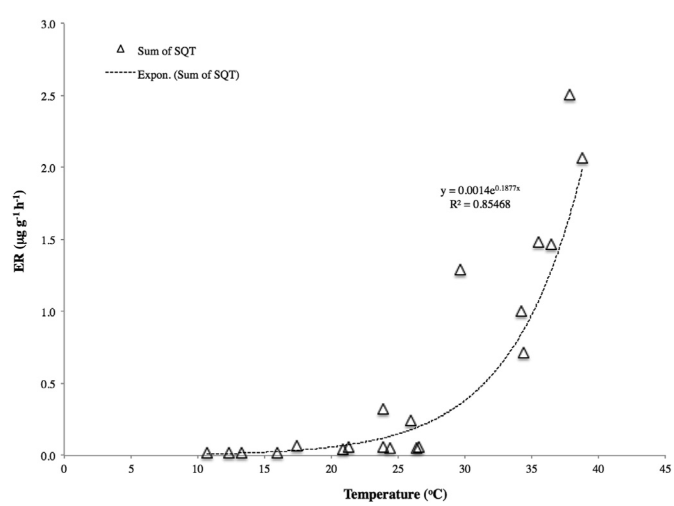

Fig. 2. Total sesquiterpene (SQT) emission rate (ER) temperature dependence based on individual hourly measurements from an Ohio buckeye tree (*Aesculus glabra* Willd.) June 23–25, 2010. Also shown is the best-fit exponential curve through the 20 data points indicating a β-factor of 0.19 K^{-1}.

Table 3
Speciation of monoterpene compounds in emission samples (% of each compound of the total monoterpene emissions).

Common name	Total MT BER ($\mu g\ g^{-1}\ h^{-1}$)	α-Pinene	Limonene	*Trans*-ocimene	Tricyclene	Camphene	Sabinene	β-Pinene	Myrcene	3-Carene	α-Terpinene	Terpinolene	*o*-Cymene	α-Thujene	*Cis*-ocimene	γ-Terpinene	Ocimene
Sugar maple	0.07 (0.02, 0.11)[a]	10	47	43													
Ohio buckeye	6.61 (1.76, 11.47)	11	41	4	5	1	14	7	10		3	4					
Northern hackberry	0.33 (0.09, 0.57)[a]		82										18				
Turkish hazelnut	1.30 (0.32, 2.23)[a]	14	29	44				7		6							
London planetree	0.15 (0.02, 0.27)[a]		90											10			
American basswood	1.50 (0.40, 2.70)[a]	51	18						12						19		
Littleleaf linden	0.71 (0.33, 1.09)[a]		72			18								10			
Valley Forge elm	0.96 (0.01, 1.92)	3	39					1				3		16		8	30
Japanese zelkova	0.42 (0.26, 0.58)[a]	35	65														

[a] For these BER, the data were not fitted to an exponential curve, rather they are reported as the median of individual sample results (with lower bound, upper bound $1-\sigma$ uncertainty window in parentheses) after normalizing each sample to 30 °C using a β of 0.10 °C^{-1} for MT.

3.2.3. Northern hackberry (*C. occidentalis L.*)

Two MT were identified in northern hackberry: *o*-cymene and limonene. The SQT α-himachalene was also tentatively identified. The temperature dependence of observed emissions was not obvious; consequently, emission rates were not fitted to an exponential curve. Rather, they are reported as the median after normalizing each sample to 30 °C using a β of 0.10 °C^{-1} for MT and 0.17 °C^{-1} for the SQT (Ortega et al., 2008). BER were determined to be 0.33 (0.09, 0.57) $\mu g\ g^{-1}\ h^{-1}$ for total MT and 0.20 (0.11, 0.30) $\mu g\ g^{-1}\ h^{-1}$ for the SQT. MT emissions in other *Celtis* spp. studied were reported as high as 0.2 $\mu g\ C\ g^{-1}\ h^{-1}$ (Benjamin et al., 1996; Nowak et al., 2002).

3.2.4. Turkish hazelnut (*C. colurna L.*)

Turkish hazelnut emitted the MT limonene, α-pinene, β-pinene, 3-carene, and *trans*-ocimene. Nonanal (C_9) and *trans*-verbenol (C_{10}) were also observed as 60% and 38%, respectively, of total other VOC emissions. The total BER was determined to be 1.30 (0.32, 2.23) $\mu g\ g^{-1}\ h^{-1}$ for MT and 0.72 (0.49, 0.95) $\mu g\ g^{-1}\ h^{-1}$ for other VOC. Nowak et al. (2002) reported an estimated MT emission rate of 0.9 $\mu g\ C\ g^{-1}\ h^{-1}$ in *Corylus* spp.

3.2.5. London planetree (*Platanus × acerifolia Aiton Willd.*)

While our sampling method was not tailored to isoprene, we were able to detect it in emissions from London planetree. Emission rates for isoprene were determined to be 0.14 (0.01, 0.29) $\mu g\ g^{-1}\ h^{-1}$, a relatively low value for isoprene emission (e.g., oak trees exhibit isoprene emission rates on the order of 700–800 times what was observed here for London planetree (Geron et al., 2001; Guenther et al., 1993; Sharkey et al., 1996)). Chang et al. (2012) reported an isoprene emission rate of 8.9 $\mu g\ C\ g^{-1}\ h^{-1}$ for London planetree in the Greater Hangzhou Area of China. Benjamin et al. (1996) reported a value of 19.2 $\mu g\ g^{-1}\ h^{-1}$ for the same species in Southern California. Limonene and α-thujene were the observed MT, and β-gurjunene was the observed SQT. Their total BER were 0.15 (0.02, 0.27) $\mu g\ g^{-1}\ h^{-1}$ and 0.11 (0.01, 0.20) $\mu g\ g^{-1}\ h^{-1}$, respectively. Other studies have reported *Platanus* spp. MT emission rates as high as 0.1 $\mu g\ C\ g^{-1}\ h^{-1}$ (Benjamin et al., 1996; Kesselmeier and Staudt, 1999; Nowak et al., 2002).

3.2.6. American basswood (*T. americana L.*)

Four MT were observed in American basswood: α-pinene, myrcene, limonene, and *cis*-ocimene, yielding a total MT BER of 1.50 (0.40, 2.70) $\mu g\ g^{-1}\ h^{-1}$. Nowak et al. (2002) estimated a MT emission rate of <0.1 $\mu g\ C\ g^{-1}\ h^{-1}$ for *Tilia* spp.

3.2.7. Littleleaf linden (*T. cordata Mill.*)

Littleleaf linden emitted the MT α-thujene, camphene, and limonene. The SQT α-himachalene was tentatively identified, as well as a C_{13} compound, α-ionone. The total BER for the MT was 0.71 (0.33, 1.09) $\mu g\ g^{-1}\ h^{-1}$, 0.13 (0.06, 0.21) $\mu g\ g^{-1}\ h^{-1}$ for the SQT, and 0.15 (0.10, 0.20) $\mu g\ g^{-1}\ h^{-1}$ for the other VOC.

3.2.8. Valley Forge elm (*U. americana L. 'Valley Forge'*)

Compounds identified in the Valley Forge elm branch enclosure samples included the MT α-thujene, α-pinene, γ-terpinene, β-pinene, terpinolene, limonene, and ocimene. Total MT BER was 0.96 (0.01, 1.92) $\mu g\ g^{-1}\ h^{-1}$. Benjamin et al. (1996) observed MT emissions below their detection limits for Valley Forge elm. Kesselmeier and Staudt (1999) reported detection of MT but no quantification. Nowak et al. (2002) estimated a MT emission rate of 0.1 $\mu g\ C\ g^{-1}\ h^{-1}$ for *Ulmus* spp.

Table 4
Speciation of sesquiterpene compounds in emission samples (% of each compound of the total sesquiterpene emissions).

Common name	Total SQT BER ($\mu g\ g^{-1}\ h^{-1}$)	Caryophyllene	α-*Trans*-bergamotene	α-Guaiene	α-Himachalene	β-Gurjunene
Sugar maple	<0.01					
Ohio buckeye	0.44 (0.06, 0.83)	19	8	73		
Northern hackberry	0.20 (0.11, 0.30)[a]				100	
Turkish hazelnut	<0.01					
London planetree	0.11 (0.01, 0.20)[a]					100
American basswood	<0.01					
Littleleaf linden	0.13 (0.06, 0.21)				100	
Valley Forge elm	<0.01					
Japanese zelkova	0.11 (0.05, 0.16)[a]					100

[a] For these BER, the data were not fitted to an exponential curve, rather they are reported as the median of individual sample results (with lower bound, upper bound $1-\sigma$ uncertainty window in parentheses) after normalizing each sample to 30 °C using a β of 0.17 °C^{-1} for SQT.

3.2.9. Japanese zelkova (Z. serrata Thunb. Makino)

Two MT, α-pinene and limonene, were identified in the Japanese zelkova emissions. A SQT, β-gurjunene, was also observed. Total BER for the MT was 0.42 (0.26, 0.58) $\mu g\ g^{-1}\ h^{-1}$ and 0.11 (0.05, 0.16) $\mu g\ g^{-1}\ h^{-1}$ for the SQT. Benjamin et al. (1996) reported a MT emission rate for this tree species of <0.1 $\mu g\ g^{-1}\ h^{-1}$.

In summary, for the BER results for all tree species included in the present study, 82% of BER were within a factor of two of emission rates for these species reported in the literature (Benjamin et al., 1996; Chang et al., 2012; Kesselmeier and Staudt, 1999; Nowak et al., 2002). Isoprene was seen in one tree species; all other tree species had isoprene emission rates that were below our detection limit of ~0.01 $\mu g\ g^{-1}\ h^{-1}$.

3.3. Modeling results

The goal of the model study was to investigate the emission changes resulting from planting one million low-VOC emitting trees using the BER of the species determined in this study. For comparison, we also ran the model on two tree species, Kermes oak and English oak, which are well-known high-BVOC emitters. While Kermes oak is a low isoprene emitter relative to other oak species, it is a high MT and SQT emitter (Karl et al., 2009; Staudt and Lhoutellier, 2011). English oak, on the other hand, is solely a high isoprene emitter (Karl et al., 2009). It grows well in Colorado, and, as such is commonly recommended for planting (Colorado State University Extension, 2013). We assumed these million trees would replace ~20% of the trees that already exist in Denver due to old age, disease, or some other cause for removal. The model ignored emissions from the remaining 80% of city trees. The model assumed that the trees planted had reached maturity. The BER for the temperature-dependent categories (MT and SQT) were obtained by taking the median of the total MT or SQT BER of each tree species included in this study. Fig. 3 presents the results of the MEGAN model simulations of the emission rates for the area of the City and County of Denver covered by one million trees (9%). The May 1–October 15, 2010 simulation period represents the seasonal period during which BVOC emissions from this deciduous vegetation are most significant (beginning approximately two weeks after bud break and ending two weeks before leaf senescence). The low emitter time series incorporates median BER values of 0.71 $\mu g\ g^{-1}\ h^{-1}$ for MT, 0.11 $\mu g\ g^{-1}\ h^{-1}$ for SQT, and 0.01 $\mu g\ g^{-1}\ h^{-1}$ (the detection limit) for isoprene, which are the median emission rates determined in the present study. For the Kermes oak species time series, MT, SQT, and isoprene emissions were calculated using BER values of 13.1 $\mu g\ g^{-1}\ h^{-1}$, 0.47 $\mu g\ g^{-1}\ h^{-1}$, and 0.1 $\mu g\ g^{-1}\ h^{-1}$, respectively. For English oak, an isoprene BER value of 70 $\mu g\ g^{-1}\ h^{-1}$ was used for the high isoprene emitter case, as reported in recent literature (Karl et al., 2009; Staudt and Lhoutellier, 2011). The integrated seasonal emission of MT, SQT, and isoprene were 17,000 kg, 1700 kg, and 160 kg, respectively, for the low emitter scenario, and 310,000 kg, 7800 kg, and 1600 kg, respectively, for Kermes oak. The integrated seasonal emission of isoprene for the English oak scenario was 1,200,000 kg. The oak isoprene emission values determined in this simulation, with a maximum flux of 5 mg $m^{-2}\ h^{-1}$ for the vegetated surface area are well within the range reported by Wiedinmyer et al. (2005). They estimated emissions as high as 16 mg $m^{-2}\ h^{-1}$ in the Ozarks Isoprene Experiment (OZIE), a study that measured and modeled isoprene emission from a region containing a high density of isoprene-emitting oak trees. Over the simulation period, MT- and SQT-modeled emissions from the low-VOC emitting tree species investigated in this work were 5% and 21%, respectively, of what emissions would have been had Kermes oak been planted instead. The low emitters' isoprene-modeled emissions were 10% of the Kermes oak case. The isoprene emissions from the low-emitting species were less than 0.02% of the high-emitting English oak projection. The total BVOC-modeled emissions from the low-emitting species were 1.6% of the projected isoprene emissions from English oak. It should be noted that the simulated estimates presented here are for comparison, an order of magnitude sensitivity estimate, and are accompanied by large uncertainties due to the aforementioned assumptions made.

In order to provide another estimate of the impact resulting from these different scenarios, the VOC emission difference was scaled to automobile emissions. Ho et al. (2009) studied VOC emitted from vehicles in a busy Hong Kong tunnel. They determined a total average emission factor of 115 mg $vehicle^{-1}\ km^{-1}$. If we convert the findings from the model in this study into equivalent total number of kilometers driven to release the same amount of VOC, then translate to the equivalent total of number of cars (assuming an average distance per vehicle drive mileage of 20,000 km per year) based on US Department of Transportation Federal Highway Administration reports (Office of Highway Policy Information, 2011), we find the following: Planting one million low-emitter trees in Denver would release 19,000 ± 12,000 kg BVOC, the same amount of VOC as 8200 cars that travel an average of 20,000 km a year. By comparison, one million Kermes oak trees would be equivalent to 140,000 vehicles on the road (320,000 kg VOC). Finally, one million English oak trees planted in Denver would yield 1,200,000 kg, the same amount of VOC released by 500,000 vehicles driving the same distance per year. Therefore, choosing the low-emitting tree species as an alternative to high-emitting trees (such as English oak) will have an effect equivalent of preventing emissions from as many as 490,000 cars from the inner city traffic. This reduction in VOC emissions, or equivalent automobile miles/number of vehicles is a remarkable figure that scales to a similar order of magnitude of emission reductions as public transportation measures implemented by city programs.

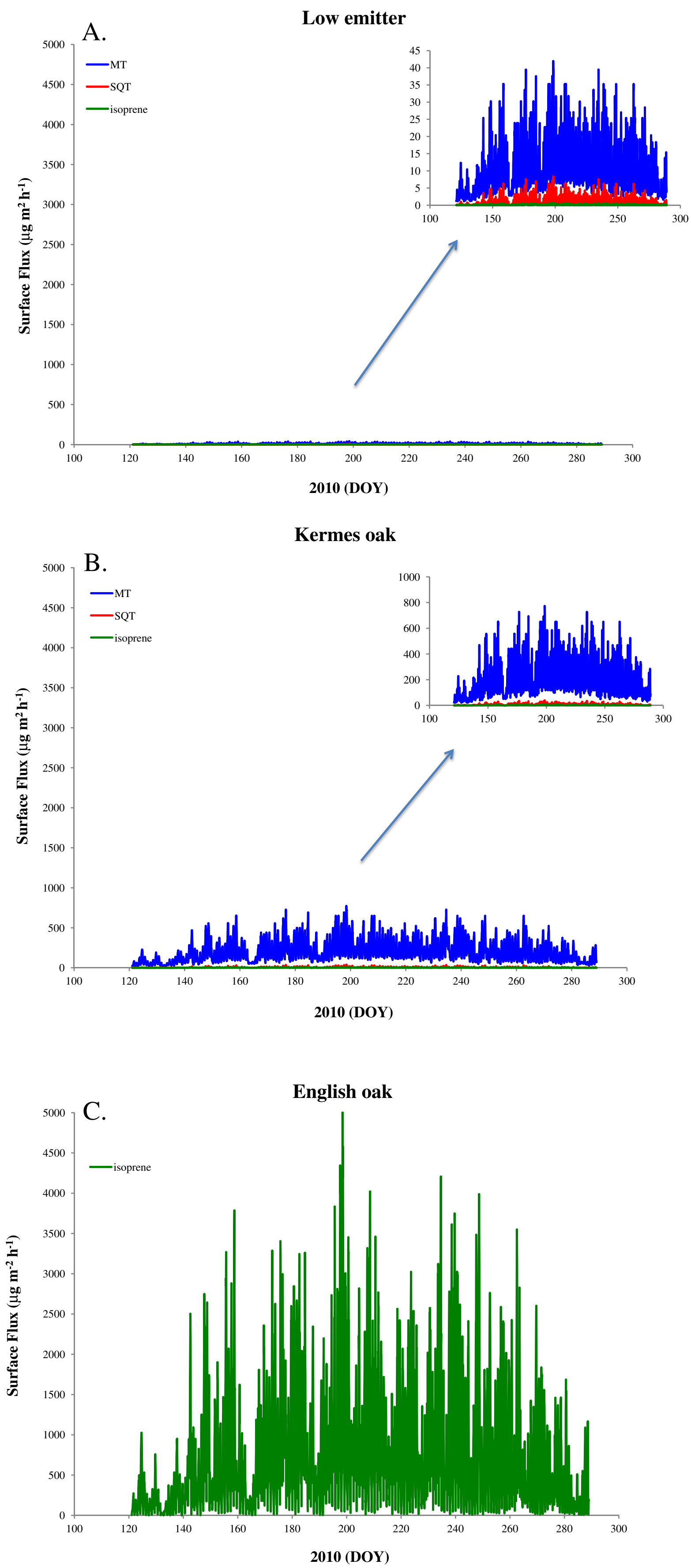

Fig. 3. A. Time series showing modeled isoprene, MT, and SQT emissions of 1 million trees covering ~9% of the surface area of the City and County of Denver during emission season, using the median result in emission rates from the low-BVOC emitting tree species that were investigated in this study. B. Time series showing modeled isoprene, MT, and SQT emissions of 1 million Kermes oak (*Q. coccifera* L.) trees covering ~9% of the surface area of the City and County of Denver during emission season. C. Time series showing modeled isoprene emission of 1 million English oak (*Q. robur* L.) trees covering ~9% of the surface area of the City and County of Denver during emission season.

4. Conclusions

BVOC emissions were identified in nine tree species chosen for planting by the City and County of Denver's Mile High Million program, and their emission rates were determined. These nine tree species were found to behave as low-to-moderate-BVOC emitters in Colorado's inner-city environment. The modeling study showed that potential emissions to the atmosphere from planting one million low-BVOC tree species would generate 19,000 kg of total VOC emissions per year. Planting these low-emitting tree species will prevent 300,000 kg and 1,100,000 kg in emissions, respectively, compared to planting the same number of high-BVOC emitting Kermes and English oak tree species, respectively. This is equivalent to removing some 490,000 cars from the City roads. The findings from this study show that use of the i-Tree database successfully facilitated selection of low-emitting tree species and the goal to improve air quality in the City and County of Denver.

These modeling results demonstrate the magnitude of emission reductions from the proper selection of tree species and underscore the value and benefit of this tool in the selection of trees. Previous studies, such as those cited in the introduction, have addressed the importance and strategies of selecting low-BVOC emitting tree species. This is the first study to validate that these tree species behave as predicted in Colorado's inner city environment. The findings from the present study can provide guidance for urban foresters and planners for selecting and planting trees that are best suited for improving air quality in the City and County of Denver and other metropolitan areas that face the challenge of maintaining air quality standards.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.atmosenv.2014.06.035.

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