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In situ emission of BVOCs by three urban woody species

Ehsan Khedive[a], Anoushirvan Shirvany[a,*], Mohammad Hassan Assareh[b], Thomas D. Sharkey[c]

[a] Department of Forestry and Forest Economics, Faculty of Natural Resources, University of Tehran, Chamran Blvd. Karaj, P.O. Box 31585-4314 Iran
[b] Institute of Medicinal Plants Technology and Development, Mola Sadra Rd, Tehran, P.O. Box 14155-1565 Iran
[c] Department of Biochemistry and Molecular Biology, Michigan State University, 603 Wilson Rd, Rm 201, East Lansing, MI 48824-1319 USA

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ABSTRACT

Controlling and monitoring air quality in cities requires understanding anthropogenic sources, but also natural sources must be considered. This is because beneficial Biogenic Volatile Organic Compounds (BVOCs) can exacerbate air pollution by reacting with anthropogenic pollutants. Although these compounds help trees survive, they may have negative effect on human life in polluted cities. In this study we measured terpenoid emissions of urban trees early and late in the growing season, using Solid Phase Micro-extraction (SPME) in a branch enclosure system. Results showed that *Robinia pseudoacacia* and *Platanus orientalis* emitted significant amounts of isoprene throughout the season. Isoprene emission early in the season was roughly the same for both species. Late in the season, the standardized emission rate increased to 17.8 and 45 $\mu g\, g^{-1}$ dw h^{-1} for *R. pseudoacacia* and *P. orientalis*, respectively. Furthermore, all trees emitted significant amounts of 2-ethylhexanol late in the season (7.3, 7.9, and 9.2 $\mu g\, g^{-1}$ dw h^{-1} for *Fraxinus rotundifolia*, *R. pseudoacacia*, and *P. orientalis*, respectively). In conclusion, trees that are typically planted in urban Tehran, emit significant amounts of isoprene. Planting more *F. rotundifolia* and fewer *P. orientalis* trees would help improve air quality in Tehran and the cities like Tehran.

1. Introduction

Urban air pollution is one of the great concerns today. Air pollution comes from anthropogenic sources but the effects can be made worse by natural emissions. The effects of directly emitted pollution, which results from atmospheric chemistry involving both anthropogenic and biogenic gases, can cause several chronic diseases (Calderón-Garcidueñas et al., 2010; Fong et al., 2010; Gurjar et al., 2010; Prioleau, 2009). Today, most of anthropogenic sources have been measured, however, the amount and role of natural sources that can affect air quality are less well known.

Although we consider urban parks and green areas to be healthy places in the heart of the cities (Yin et al., 2011), they can exacerbate the pollution in some circumstances by emission of Biogenic Volatile Organic Compounds (BVOCs). The type of vegetation cover, species composition, and exposure to pollutants (i.e. NO_x, OH, O_3) are determinant factors of the role of these BVOCs (Hellén et al., 2012).

Isoprenoids are among the most diverse BVOCs that plants produce, some of them are vital to the plant's life while others are emitted to earth's atmosphere as secondary metabolites (Ro, 2011). These secondary metabolites may have positive effects on both the plants that emit them and humans who are exposed to (Lee et al., 2011; Li et al., 2011). Among these compounds, isoprene (C_5H_8), the root member of the isoprenoids, has the highest emission rate from vegetation cover, especially trees, to the atmosphere (Guenther et al., 2012; Sharkey and Monson, 2014).

Although isoprenoids have positive functions in plant life, these compounds and their oxidation derivatives have significant impacts on secondary organic aerosol formation and tropospheric ozone (Dani et al., 2014). Studies on reactions of terpenes with ozone in air demonstrated the production of hydrogen peroxide (Becker et al., 1990), sulfuric acid (Kotzias et al., 1990), hydroxyl radicals (Forester and Wells, 2011), and secondary aerosols (Lamorena and Lee, 2008; Saraga et al., 2010; Yokouchi and Ambe, 2007).

Among the isoprenoids, the importance of isoprene itself in atmospheric chemistry and pollution is well known. Isoprene/ozone mixtures in the atmosphere results in a higher reduction of respiratory rate of mice compared with α-pinene and D-limonene (Wilkins et al., 2001; Wolkoff et al., 2000). Isoprene

* Corresponding author.
E-mail addresses: e.khedive@ut.ac.ir (E. Khedive), Shirvany@ut.ac.ir (A. Shirvany), asareh@gmail.com (M.H. Assareh), tsharkey@msu.edu (T.D. Sharkey).

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emission from plants in regions with NO_x and OH in the air leads to ozone formation (Curci et al., 2009; Duane et al., 2002; Geng et al., 2011; Hewitt et al., 2011). Further, the reaction of isoprene and terpenoids with ozone leads to formation of airborne ultrafine nanoparticles (Rohr et al., 2003). Therefore, investigation of influential parameters on its production from plants is of major concern, especially with the likely higher emission rate in the near future, as a result of climate change (Sharkey and Monson, 2014).

Isoprene is emitted mostly from plants but there are also anthropogenic sources. Isoprene is a major part of the hydroxyl radical reactivity of air masses (Hellén et al., 2012). The negative effect of isoprene on air quality is exacerbated in urban environments where NO_x, and OH has higher concentrations compared to neighboring areas. On the other hand, urban green areas are irrigated regularly, and if the plants undergo water stress like what happens in nature, isoprene emission capacity reduces significantly (Brilli et al., 2013; Rodríguez-Calcerrada et al., 2013), however, after re-irrigation, their isoprene emission might be increased several fold relative to what it was before the stress (Sharkey and Loreto, 1993).

In Tehran city, downtown streets have high percent of green areas covered by trees. About 70% of the trees are *Platanus orientalis* (Pourhashemi et al., 2012), and the earthy smell of isoprene can be recognized in hot sunny summer days in some streets. Hence, measurement of isoprene and other terpenoid emissions in urban green areas is of great concern. We studied in situ emission of terpenoids by *Platanus orientalis* L. (this point forward mentioned as *P. orientalis*), *Fraxinus rotundifolia* Miller (this point forward mentioned as *F. rotundifolia*), and *Robinia pseudoacacia* L. (this point forward mentioned as *R. pseudoacacia*), the three most common trees in urban areas of Iran (especially Tehran).

2. Materials and methods

2.1. Site description and sampling

Field experiments were conducted at Forest and Rangeland Institute, Karaj city located in Alborz province (30 km from downtown Tehran), Iran during summer 2014. Climate of the study site is classified as semi-arid according to Peel et al. (2007) with mean annual temperature of 17.4 °C and annual precipitation of 233 mm. The most common trees in the institute yard were *F. rotundifolia*, *R. pseudoacacia*, and *P. orientalis*. All the trees were healthy and even-aged, roughly 40 years old, and irrigated regularly by the institute, but no pruning treatments were done on them. Three trees of each species were selected for sampling, and measured for three consecutive days (one tree of each species in each day) between 12 noon and 5 p.m. Measurements were done in two time periods: 1- early in the season when the leaves are young (mid-July), and 2- late in the season when the leaves are over mature (late-October).

2.2. Measurements protocols

Samples were taken using 75 μm portable field sampler Solid Phase MicroExtraction (SPME) (SUPELCO®) (Carboxen/polydimethylsiloxane coating) in a branch enclosure system with a fixed air flow rate. Branches were enclosed at 2 m above the ground in a cuvette with a volume of 30 L, which was equipped with inlet and outlet ports. Sampling with SMPE was done at the outlet of the cuvette. Air flow was provided using a dry air pump with a flow of 3 L min^{-1}. Pollutants and ozone were removed using a combination filter of activated charcoal and potassium iodide (Merck) (Brown et al., 2008; Holzke et al., 2006; Schuh et al., 1997). Along with sampling, chamber air temperature and leaf temperature (using an infrared thermometer) and Photosynthetic Active Radiation (PAR) were measured. We let SPME absorb compounds for 30 min. After measurements, leaves were detached from the branches and dried in an oven (70° C for 24 h) for calculation of isoprene and 2-ethylhexanol emission rates based on leaf dry weight.

PAR data were calculated according to Wang et al. (2013) by gathering global radiation (GR) data (measured each two seconds during day) from a nearby synoptic station during the measurement hours.

2.3. GC-mass analysis

Samples were taken each day to the laboratory to both analyze the compounds and prepare SPME for next sampling. Sample analysis was performed using an Agilent GC (6890N) – mass spectrometer (5973N) (Hewlett-Packard USA) equipped with DB–5 ms column (30 m × 0.25 mm i.d., 0.25 μm film thickness) with the temperature program according to Cheng et al. (2009). For quantitative analysis, an isoprene standard was made by vaporizing isoprene standard (SIGMA-ALDRICH) in gas flask filled with pure nitrogen, and then the gas was sampled using SPME to exclude partition coefficient calculations of SPME. 2-ethylhexanol was quantified using GC/MS response factors between isoprene and 2-ethylhexanol. Limit of detection for isoprene and 2-ethylhexanol was calculated as 3.12 and 1.87 ng respectively.

All measurements were standardized to 30 °C and 1000 μmol m^{-2} s^{-1} according to Guenther et al. (1993).

3. Results

3.1. Qualitative results

Results of mass spectrometry on terpenoids identification showed that throughout the sampling, none three tree species emit monoterpenes and sesquiterpens steadily. In the early season, only isoprene was detected as a regularly emitted BVOC in *P. orientalis* and *R. pseudoacacia* (Fig. 1). No isoprene emission was detected from the *F. rotundifolia*. All other BVOCs were detected only in some trees in that sampling phase and had very low emission rates (Table 1). One of *F. rotundifolia* trees emitted significant amounts of ocimene in early season phase, but no emission was observed in late season. Interestingly, none of the trees emitted 2-ethylhexanol in the early season (at detectable levels), however, late in the season this was the only BVOC among all three species (Fig. 2).

3.2. Isoprene emission capacity

An isoprene emission boxplot of two tree species early and late in the season is shown in Fig. 3. The mean standardized isoprene emission of *R. pseudoacacia* was 0.8 and 17.8 μg g^{-1} dw h^{-1} and that of *P. orientalis* was 1.5 and 45 μg g^{-1} dw h^{-1} early and late in the season, respectively. No emission was detected from the *F. rotundifolia* (at the detection limits). In both species some trees did not emit isoprene at the detection limits in the evening. Both species have considerably lower emission rates early in the season. In late sea-

Table 1
Detected compounds emitted from each species. All compounds, except isoprene and 2-ethylhexanod did not have steady emissions.

Species	Early season emission	Late season emission
Fraxinus rotundifolia	Ocimene†, Myrtanal	2-ethylhexanol, Limonene
Robinia pseudoacacia	Isoprene*, Amorphane, trans-pinane, Bergamotane	Isoprene*, 2-ethylhexanol*, 3-carene
Platanus orientalis	Isoprene*, β- citronellol	Isoprene*, 2-ethylhexanol*, Limonene

* These compounds emitted by all the trees of the species in corresponding season.
† This compound emitted in various isomers.