DOKUZ EYLÜL UNIVERSITY
GRADUATE SCHOOL OF NATURAL AND APPLIED SCIENCES

BIOGENIC VOLATILE ORGANIC COMPOUNDS (BVOCs) EMISSIONS FROM THE FORESTED AREAS IN TURKEY: DETERMINATION OF EMISSION FACTORS FOR ENDEMIC TREE SPECIES

by
Barış YAMAN

December, 2013
İZMİR

BIOGENIC VOLATILE ORGANIC COMPOUNDS (BVOCs) EMISSIONS FROM THE FORESTED AREAS IN TURKEY: DETERMINATION OF EMISSION FACTORS FOR ENDEMIC TREE SPECIES

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Barış YAMAN

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M.Sc THESIS EXAMINATION RESULT FORM

We have read the thesis entitled **"BIOGENIC VOLATILE ORGANIC COMPOUNDS (BVOCs) EMISSIONS FROM THE FORESTED AREAS IN TURKEY: DETERMINATION OF EMISSION FACTORS FOR ENDEMIC TREE SPECIES"** completed by **BARIŞ YAMAN** under supervision of **PROF. DR. MUSTAFA ODABAŞI** and we certify that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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ABSTRACT

Emission factors of biogenic volatile organic compounds (BVOCs) from seven endemic tree species (*Abies nordmanniana* subsp. *equi-trojani*: Troy Fir, *Abies nordmanniana* subsp. *bornmuelleriana*: Uludag Fir, *Abies cilicica* subsp. *isaurica*: Cilician Fir, *Liquidambar orientalis*: Oriental Sweetgum, *Quercus macranthera* subsp. *syspirensis*: Ispir Oak, *Quercus aucheri*: Boz Pirnal Oak and *Quercus vulcanica*: Vulcanic Oak) grown in Turkey were determined. A dynamic enclosure system was used to sample BVOCs where a branch was enclosed in a transparent Nalofan bag, maintaining natural conditions and avoiding any source of stress. Two branches of three different trees were sampled to produce average BVOC emission factors for each species. All meteorological and environmental parameters (temperature, relative humidity, Photosynthetically Active Radiation [PAR] and carbon dioxide) inside the chamber and in air were monitored and recorded. BVOCs were collected on adsorbent tubes (Tenax) from the inlet and outlet of the chamber. Sixty five BVOCs (in five groups: isoprene, monoterpenes, sesquiterpenes, oxygenated sesquiterpenes and oxygenated compounds) were analyzed with GC/MS. All emission factors were normalized to standard conditions. Isoprene was the prominent compound for Cilician Fir, Vulcanic Oak, Ispir Oak and Oriental Sweetgum while the others emitted mainly monoterpenes. Quantitatively, Ispir Oak, Oriental Sweetgum and Cilician Fir were the highest BVOC emitters while Boz Pirnal Oak had the lowest emission rate. Oxygenated compounds were the third most prominent BVOC group and sesquiterpenes had slightly lower contributions. As mostly reported in the literature, coniferous and broad-leaved species emitted predominantly monoterpenes and isoprene, respectively.

Keywords: BVOC emissions, dynamic enclosure system, endemic tree, emission factor, Turkey.

TÜRKİYE'DE BİYOJENİK UÇUCU ORGANİK BİLEŞİK EMİSYONLARI: ENDEMİK AĞAÇ TÜRLERİ İÇİN EMİSYON FAKTÖRLERİNİN BELİRLENMESİ

ÖZ

Türkiye'de yetişen yedi endemik ağaç türü (*Abies nordmanniana* subsp. *equi-trojani*: Kazdağı Göknarı, *Abies nordmanniana* subsp. *bornmuelleriana*: Uludağ Göknarı, *Abies cilicica* subsp. *isaurica*: Toros Göknarı, *Liquidambar orientalis*: Anadolu Sığlası, *Quercus macranthera* subsp. *syspirensis*: İspir Meşesi, *Quercus aucheri*: Boz Pırnal Meşesi ve *Quercus vulcanica*: Kasnak Meşesi) için biyojenik kökenli uçucu organik bileşik (BVOC) emisyonları belirlenmiştir. Örneklemelerde dinamik test odası tekniği kullanılmıştır. Ağacın seçilen bir dalı, şeffaf Nalofan bir torba içine alınarak ağaç için herhangi bir stres kaynağı oluşturmadan torba içinde doğal çevresel şartların oluşması sağlanmıştır. Örneklemeler, her türü temsilen seçilen üç farklı ağacın iki farklı dalında gerçekleştirilmiştir. Meteorolojik ve çevresel koşullar (sıcaklık, nem, fotosentetik aktif radyasyon [PAR] ve karbondioksit) örneklemeler boyunca test odası içinde ve dış havada ölçülmüş ve kaydedilmiştir. BVOC örnekleri test odası giriş ve çıkışından adsorban tüplerle (Tenax) toplanmış ve GC/MS ile analizlenmiştir. Toplam altmışbeş BVOC türü için (beş grupta: isopren, monoterpenler, sesquiterpenler, oksijenli bileşikler ve oksijenli sesquiterpenler) emisyon faktörleri belirlenmiştir. Sonuçlar standart şartlara göre düzeltilmiştir. Toros Göknarı, Kasnak Meşesi, İspir Meşesi ve Anadolu Sığlası'ında isoprenin, diğerlerinde ise monoterpenlerin yüksek olduğu görülmüştür. Toplam emisyon faktörleri ise; İspir Meşesi, Anadolu Sığlası ve Toros Göknarı'nda en yüksek, Boz Pırnal Meşesi'nde en düşük olarak belirlenmiştir. Oksijenli bileşikler en çok görülen üçüncü grup iken, sesquiterpenler çok daha düşük oranlarda kalmıştır. Literatürde de sıkça rapor edildiği gibi geniş yapraklı türlerin isopren, ibreli türlerin ise monoterpen yayınlama eğiliminde olduğu belirlenmiştir.

Anahtar Kelimeler: BVOC emisyonları, dinamik test odası, endemik ağaç, emisyon faktörü, Türkiye.

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CHAPTER ONE
INTRODUCTION

1.1 Introduction

It is now widely acknowledged that biological processes in terrestrial ecosystems broadly affect the atmosphere and climate of Earth, which consequently implies potentially significant feedback effects on current global changes in atmosphere and climate arising from human activities (Penuelas, Rutishauser, & Filella, 2009). Of these biological processes, those related to the carbon cycle (e.g. the assimilation and release of CO_2 and the carbon sequestration in organic material) have been the focus of much attention (Laothawornkitkul, Taylor, Paul, & Hewitt 2009). However, gases other than CO_2 are exchanged between the biosphere and the atmosphere. Vegetation covering the landmasses releases biogenic volatile organic compounds (BVOCs), those comprise a large variety of molecules that differ in size and physicochemical properties as well as in their metabolic origin (Kesselmeier & Staudt, 1999). Plants synthesize these compounds via several biochemical pathways, those have been the subject of much recent research with many uncertainties still discussed (Fall, 1999; Fuentes et al., 2000). The functions of these emissions in plant metabolism, growth, reproduction, protection, defense and communication will evidently be altered by the changes arising from global and climate changes, and as a result of these alterations, the structure and the functioning of organisms, communities and ecosystems might therefore change significantly (Penuelas & Staudt, 2010). At present, a total of 1700 volatile organic compounds have been identified from more than 90 plant families (Knudsen & Gershenzon, 2006). These volatiles constitute about 1% of plant secondary metabolites known to date and are mainly represented by terpenoids, phenylpropanoids/benzenoids, fatty acid and amino acid derivatives (Dudareva, Pichersky, & Gershenzon, 2004). Volatile organic compounds are typically lipophilic liquids with high vapor pressures and can cross membranes freely and be released into the atmosphere or soil in the absence of a diffusion barrier (Pichersky, Noel, & Dudareva, 2006).

Vegetative emissions have been discussed as the main subject in many studies while their significance has been realized in recent years. BVOCs; including isoprene, terpenes (monoterpenes, sesquiterpenes) and oxygenated compounds (alcohols, aldehydes, ketones, acetates) are important for atmospheric chemistry, since they contribute to secondary organic aerosol formation and play an important role in the oxidative capacity of the atmosphere (Andreae & Crutzen, 1997; Fuentes et al., 2000). Furthermore, because of their high reactivities, BVOCs have effects on the chemical composition and physical characteristics of the atmosphere as they photochemically react with nitrogen oxides (NO_X) and causing tropospheric ozone formation (Simpson, 1995; Bonn & Moortgat, 2003; Joutsensaari et al., 2005; Fares et al., 2011). All these adverse impacts made BVOCs become a current issue and thus incented several researchers to determine their qualifications and quantifications in the atmosphere for the purpose of setting up air pollution control strategies (Padhy & Varshney, 2005; Filella & Penuelas 2006). As previously assigned, the fact "BVOCs have a higher ratio than the anthropogenic VOCs in the earth atmosphere", clearly emphasizes the seriousness of the case (Guenther et al., 1995).

Leaf/needle, branch, canopy or ecosystem level measurements with various methods and equipments have been conducted to determine the biogenic emissions in global or regional scales all over the world (Guenther et al., 1996; Singsaas & Sharkey, 2000; Greenberg et al., 2004; Helmig, Bocquet, Pollmann, & Revermann, 2004; Holzke, Hoffmann, Jaeger, Koppmann, & Zimmer, 2006; Matsunaga et al., 2011; Baghi, Helmig, Guenther, Duhl, & Dali, 2012; Matsunaga et al., 2013). Vegetative emission profile of an interested region is mostly obtained by using the species-specific emission factors of the dominating plant species native to the region determined with leaf/needle or branch level measurements either on-site or in laboratory (Komenda, Parusel, Wedel, Koppmann, 2001; Padhy & Varshney, 2005; Ortega & Helmig, 2008; Matsunaga et al., 2011; Baghi et al., 2012; Matsunaga et al., 2013). Then the emission factors are scaled up with the vegetative land cover data and meteorological parameters as well as modeled and eventually estimated long-term (i.e. annual) fluxes (Chang, Chen, & Huang, 2005; Sakulyanontvittaya et al., 200; Zemankova & Brechler, 2010). In previous studies, BVOC emission factors of

numerous plant species including largely common and several site-specific (endemic) species were determined and the attention was generally focused on trees, as the most substantial component of vegetation (Owen et al., 1997; Tambunan et al., 2006; Raisanen, Ryyppo, & Kellomaki, 2009; Fares et al., 2011). Endemism was clearly described by Morrone (1994) as; an ecological state of being unique to a defined geographic location, such as an island, nation or other defined zone, or habitat type. Organisms that are indigenous to a place are not endemic to it if they are also found elsewhere. And thereby, getting knowledge on emitting behaviors of endemic trees come into prominence for regional BVOC estimation and inventorying studies.

Forest areas cover 31.1% of the earth's surface and also 28% of Turkey's surface which equals to 21.7 million hectares (World Bank, 2010; GDF, 2012) making them significant BVOC sources. Therefore, specifying the emission factors of the trees composing the forests is crucial. Wilske et al. (2007) investigated isoprenoid emissions of eight tropical tree species of Southeastern Asia, and also Bao et al. (2008) screened ten Japanese plants for their biogenic emissions and many other species were investigated within numerous of studies and several well-organized BVOC measurement projects such as; ECHO (Emission and Chemical Transformation of Biogenic Volatile Organic Compounds) (Spirig et al., 2005), BEMA (Biogenic Emissions in the Mediterranean Area) (Versino, 1997). A large number of plant species with many of endemics were studied in these studies and the emission factors are available on the relevant databases. However, there is no study that directly focused on BVOC emissions in Turkey's forest areas and emissions of tree species endemic to Turkey. Although most of the common species' emission factors may be obtained from literature, there is no value reported for endemic trees of Turkey.

Getting knowledge on vegetative emissions of endemic species (that do not naturally grow in any other region) in a selected region may be very important to provide information in local air composition. Japanese Cedar (*Cryptomeria japonica*) and Bamboo-leaf Oak (*Quercus myrsinaefolia*) were examined for their monoterpene

and isoprene emissions by Bao et al. (2008). Three endemic Mexican trees; Sacred Fir (*Abies religiosa*), Netleaf Oak (*Quercus rugosa née*) and Patula Pine (*Pinus patula*) were also investigated for their isoprene and monoterpene emissions by Dominguez-Taylor, Ruiz-Suarez, Rosas-Perez, Hernandez-Solis, & Steinbrecher (2007) to guide the future biogenic emission inventories for the Mexico City area. However, there is no study that directly focused on BVOC emissions from Turkey's forest areas. The objective of this study was to determine the normalized BVOC (isoprene, monoterpenes, sesquiterpenes, oxygenated sesquiterpenes and oxygenated compounds) emission factors [at 1000 $\mu mol\ m^{-2}\ s^{-1}$ Photosynthetically Active Radiation (PAR) and 30°C temperature] from seven endemic tree species in Turkey. Seven tree species (*Abies nordmanniana* subsp. *equi-trojani*: Troy Fir, *Abies nordmanniana* subsp. *bornmuelleriana*: Uludag Fir, *Abies cilicica* subsp. *isaurica*: Cilician Fir, *Quercus aucheri*: Boz Pirnal Oak, *Liquidambar orientalis*: Oriental Sweetgum, *Quercus macranthera* subsp. *syspirensis*: Ispir Oak and *Quercus vulcanica*: Vulcanic Oak) were investigated by conducting on-site measurement campaigns in seven different regions.

CHAPTER TWO
LITERATURE REVIEW

This chapter presents information on definition, sources, and effects of BVOCs on the atmosphere, dynamic enclosure system and the other BVOC measurement methods. Previous studies for BVOC emissions of different plant species and estimation of BVOC emissions were also discussed.

2.1 BVOCs in Earth Ecosystem

2.1.1 Definition and Sources

The term "BVOC" refers to organic atmospheric trace gases other than carbon dioxide and carbon monoxide, which are based on diverse bio-chemical reactions and metabolic processes in biosphere, and include the isoprenoids (isoprene and monoterpenes) as well as alkanes, alkenes, carbonyls, alcohols, esters, ethers, and acids (Kesselmeier & Staudt, 1999). Under these groups; large number of volatile chemicals synthesized by various plants were identified (Pichersky, Noel, & Dudareva, 2006) and it is possible that the number may increase as more plants are examined with new methods. Isoprene and monoterpenes are the most prominent BVOCs and sesquiterpenes appear to be of less, though some studies report emission rates on the order of those known for isoprenoids whose carbon skeletons are composed of C5 units (Lamb, Guenther, Gay, & Westberg, 1987; Mccaskill & Croteau, 1995; Simpson et al. 1999; Scott & Benjamin, 2003; Sakulyanontvittaya et al., 2008). Isoprenoids subdivided into hemiterpenes (C5, e.g., isoprene), monoterpenes (C10, e.g., α-pinene, β-pinene, sabinene), sesquiterpenes (C15, e.g., β-caryophyllene, abscisic acid), diterpenes (C20, e.g., phytole, tocopherole, retinol), triterpenes (C30, e.g., sterols, saponins), etc. according to their C5 units. Usually these compounds are strong smelling, hardly soluble in water, and found in plants as well as in animals and microorganisms. The group of monoterpenes comprises acyclic, and mono-, bi-, and tricyclic structures; they may exist as hydrocarbons with or without the inclusion of

oxygen in compounds such as menthol, camphor, linalool, and geraniol. Oxygenated monoterpenes and their derivatives are often classified as monoterpenoids (Kesselmeier & Staudt, 1999).

BVOCs are synthesized by plants through various complex enzymatic reactions and bio-chemical pathways (Kesselmeier & Staudt, 1999; Dudareva, Negre, Nagegowda, & Orlova, 2006; Matsui, 2006; Xiang, Milc, Pecchioni, & Chen, 2007; Laothawornkitkul et al., 2009). Several studies have focused on these complicated biosynthesis mechanisms to understand of the relevant chemical or bio-chemical reactions underlying and controlling these processes (Fall, 1999; Dudareva et al., 2006; Matsui, 2006; Pichersky, Noel, & Dudareva, 2006; Sharkey, Wiberley, Donahue et al. 2008; Sharkey, 2012). Even then, there are still gaps in current knowledge of those sophisticated vegetational behaviors. Plants synthesize BVOCs in their various cellular organelles, but then they are stored in specialized secretory structures, thus protecting the plant's metabolic processes from their toxic effects. They are released from above- and below-ground plant organs. In general, flowers and fruits release the widest variety of BVOCs, with emission rates peaking on maturation but leaves have the greatest mass emission rates (Knudsen, Eriksson, Gershenzon, & Stahl, 2006; Soares, Pereira, Marques, & Monteiro, 2007; Laothawornkitkul et al., 2009). Some of the plant volatiles (e.g. methyl salicylate, hexenal or terpenes) may act as defence compounds against pathogens and herbivores, and others (e.g. methyl jasmonate, alkenes, (E)-3-hexen-1-ol or terpenes) as signals between different parts of the same plant, between plants, and between plants and animals and micro-organisms (Farmer & Ryan, 1990; Langenheim, 1994; Penuelas, Llusia, & Estiarte, 1995; Lerdau, Guenther, & Monson, 1997). Other previously addressed potential functions of BVOCs such as isoprene and terpenes are the stabilization and protection of plant membranes against high temperatures or the alteration of flowering in nearby plants. Some others (e.g. linalool) take part in attracting the pollinators (Pellmyr, Tang, Groth, Bergstrom, & Thien, 1991; Tingey, Turner, & Weber, 1991; Knudsen & Tollsten 1993; Sharkey & Singaas 1995; Terry, Stokes, Hewitt, & Mansfield, 1995; Loreto, Forster, Durr, Csiky, & Seufert, 1998).

Little is known about the regulation of BVOC synthesis rates, with probably more than 90% of the genes involved in their biosynthesis is still unidentified. There is evidence suggesting that BVOC biosynthesis is largely controlled at the level of gene expression (Hermsmeier, Schittko, & Baldwin, 2001; Kant, Ament, sabelis, Harimng, & Schuurink, 2004; Ralph et al., 2006). The changes in expression of the genes involved in BVOC synthesis positively correlate with their emission rates, and this control leads to the spatial (local and systemic) and temporal pattern in their emissions (Dudareva et al., 2003; Arimura, Huber, & Bohlmann, 2004; Underwood et al., 2005). However, abiotic stresses; including water stress, light intensity, temperature and nutrient availability, and biotic stresses; such as pathogens, herbivores and even other plants may also induce the production of some BVOCs, such as terpenes, methyl jasmonate and methyl salicylate, from leaves, the magnitude and quality of which depend on the type of damage (Takabayashi, Dicke, & Posthumus, 1994; Seo et al., 2001; Mithofer, Wanner, & Boland, 2005; Laothawornkitkul et al., 2008). Kegge & Pierik (2010) particularly surveyed the impacts of plant competitions for resources (e.g. light, water, nutrients) on BVOC emissions. On the other hand, BVOCs are produced on many different timescales. Minute-to-minute changes in the formation of BVOCs might occur as a result of environmental changes, such as rapid variation of light intensity in a forest canopy, for example formation of the hexenal family VOCs can also occur within a few minutes of wounding or physical damage (Fall, 1999). Day-to-day changes in the emissions of most VOCs are controlled by both biological processes and the physical environment. Thus, diurnal cycles of emissions of isoprene, 2-methyl-3-buten-2-ol, monoterpenes, and methanol from forest canopies are seen in response to changing light or temperature (Fall, 1999).

2.1.2 Effects on the Atmosphere

The first global estimates of BVOC release were initiated more than 50 years ago by Went (1960), and 175 Tg C yr^{-1} was considered as the first value. Rasmussen & Went (1965) later increased the estimate to 200–400 Tg C yr^{-1}. These early investigations already pointed out the significance of biogenic

emissions for atmospheric chemistry. Several studies exist reporting the BVOC amounts released from vegetation to the atmosphere. The most recent amount that was reported by Guenther et al. (1995) for total BVOC emissions is 1150 Tg C yr^{-1} (Robbins & Robinson, 1968; Rasmussen & Khalil, 1988; Turner et al., 1991; Muller, 1992; Guenther et al., 1995; Taylor, Zimmerman, & Ericikson, 1996). Although many BVOC species have been identified from plants as mentioned above, much of the global flux and subsequent effect on atmospheric chemistry is probably caused by a relatively small number of compounds (Dudareva et al., 2003). Isoprene makes the largest contribution, followed by the monoterpenes (Levis, Wiedinmyer, Bonan, & Guenther, 2003; Laothawornkitkul et al., 2009). However, sesquiterpenes are important precursors to secondary organic aerosols while estimating their emission rates is difficult because of their reactivity and low vapor pressures (Bonn & Moortgat, 2003).

BVOCs seem to influence the oxidizing potential of the troposphere and their degradation entails the formation of tropospheric ozone, which is a key pollutant in photochemical smog events and the third most important greenhouse gas after CO_2 and methane (Chameides, Lindsay, Richardson, & Kiang, 1988; Calfapietra, Fares, & Loreto, 2009; Penuelas & Staudt, 2010). The addition of O_3 to carbon–carbon double bonds leads to the formation of ozonides, which are unstable and undergo rapid decomposition. This can generate organic free radicals that can form OH and RO_2, so mediating the O_3 budget of the troposphere (Laothawornkitkul et al., 2009). These reactions also lead to formation of other secondary pollutants such as peroxyacyl nitrates (PAN), aldehydes and ketones, hydrogen peroxide (H_2O_2) (Fuentes et al., 2000). Additionally, because of many of these products are water soluble, they may be removed from the atmosphere by wet deposition or may have lower vapor pressures than the primary compounds and hence sorbed by the particles (solid or aerosol) and be removed from the atmosphere by wet or dry deposition (Fehsenfeld, 1992).

Diurnal photochemical mechanisms are mainly conducted by hydroxyl radicals (OH) and BVOC oxidations are occurred by these processes (Fuentes et al., 2000).

The primary products of BVOC-OH reactions are peroxy radicals (RO_2) and in the presence of sufficient nitrogen oxides (NO_X) these radicals can oxidize NO to NO_2, which may then leading to generation of O_3. However, at night, the concentration of another radical species: nitrate radical (NO_3), may increase considerably because of its short lifetime in sunlight and rapid reaction with NO (Atkinson & Arey, 2003). Consequently, at night, when the OH concentration is zero BVOC oxidations are mainly dominated by NO_3, even so, the primary route of oxidation of BVOCs is reaction with OH since the reaction rate of many BVOCs with NO_3 is relatively low (Lelieveld et al., 2008).

While BVOCs essentially affect the gas-phase atmospheric chemistry, they can also lead to formation of secondary organic aerosols which directly affect climate by scattering solar radiation. They also indirectly alter the Earth's radiative balance by acting as cloud condensation nuclei, changing cloud albedo and the degree of cloud cover, so potentially leading to net cooling of the Earth's surface during the day (Laothawornkitkul et al., 2009). Although, Joutsensaari et al. (2005) were noticed that BVOC oxidation products generally have lower vapor pressures than the primary compounds, and therefore they may condense more readily on pre-existing molecular clusters/particles, the mechanisms by which BVOC oxidation may lead to secondary organic aerosols in clean air are still not fully understood (Kulmala, 2003).

2.2 BVOC Emission Measurement Methods

2.2.1 Dynamic Enclosure Method

As a result of their chemical and physicochemical characteristics and complicated biological synthesizing mechanisms, measuring the plant based BVOC emissions is a substantially difficult task. Vegetation enclosure method is the most frequently referred technique in the literature (Boissard, Cao, Juan, Hewitt, & Gallagher, 2001; Harrison et al., 2001; Kim, 2001; Sabillon & Cremades, 2001; Villanueva-Fierro, Popp, & Martin, 2004; Padhy & Varshney,

2005; Holzke et al., 2006; Wilske et al., 2007; Tani & Kawawata, 2008). In this method, a leaf/needle, branch or a whole plant is enclosed in a chamber. The main requirements for an enclosure system are to maintain inside-chamber conditions (e.g. temperature, CO_2 concentration, humidity, PAR) similar to ambient air. Despite the main principal of the method is invariable, most researchers have constructed their own apparatus and follow methods unique to their laboratories (Ortega & Helmig, 2008).

Air circulation is an essential requirement for vegetation enclosure systems to prevent unsteady CO_2 concentrations and excessively increasing the inside-air temperatures. In static enclosures (Fukui & Doskey, 2000) no purge air is flushed into the chamber, hence elevated temperatures and non-realistic CO_2 concentrations create artificial conditions, which are not appropriate for measuring naturally occurring emission rates. It is also now well recognized that short-term, stress-related emissions bursts often occur soon after enclosure set up (Ortega & Helmig, 2008). Because of those disadvantages discussed above, static enclosure systems are not used in related studies anymore. Growth chambers can enclose entire plants, and are useful for controlling environmental conditions such as light, temperature, CO_2, and H_2O. They typically have a fixed volume and need to be larger in order to accommodate the pot, soil, and stem portion of the enclosed vegetation (Kempf, Allwine, Westberg, Claiborn, & Lamb, 1996). Therefore, enclosure volumes and flow rates can be very large, resulting in lower biomass/volume ratios and lower BVOC concentrations than in branch enclosures or leaf cuvettes. For instance, Bao, et al. (2008) measured BVOC emissions from 10 Japanese plant species which were planted in 10 L plastic pots, in a closed growth chamber with a volume of 8 800 L (see Figure 2.1) and the samples were collected with a flow-rate of 100 mL min^{-1}. These conditions make quantitative chemical analysis of emissions more difficult and another point of consideration is that releases from the soil can contribute to observed emissions (Ortega & Helmig, 2008). Leaf cuvette, on the other side, is another enclosure method with the smallest volume, as illustrated in Figure 2.2. In general, leaf cuvettes are commercially compacted with portable gas-exchange systems and designed for photosynthesis studies (Harley, Guenther, & Zimmerman

et al. 1995; Geron, Harley, & Guenther, 2001), but with some modifications, they can also be used for BVOC emission measurements. Usually, temperature and PAR can be automatically controlled in leaf cuvette enclosures and thereby reaching the target temperature in several minutes in such a small volume is prevented. The resulting high concentrations and negligible analyte losses typically make leaf cuvettes suitable for studying temperature and light effects on isoprene emissions (Guenther, Monson, & Fall, 1991; Harley, Guenther, Zimmerman, 1995; Geron, Harley, & Guenther, 2001). However, because of the relatively smaller amount of biomass enclosed in a cuvette and lower monoterpene and sesquiterpene emission rates, it is difficult to obtain sufficient quantities of these compounds for their chemical analysis.

Figure 2.1 The growth chamber used by Bao et al. (2008).

Figure 2.2 Application of a leaf cuvette system (Harley et al., 2004).

Dynamic enclosure method was clearly described by Ortega &Helmig (2008) as the most reasonable technique to get accurate results in biogenic emission studies. The emission rate from a dynamic enclosure is calculated by;

$$\varepsilon = \frac{(C_{out} - C_{in}).Q.t}{m_{dry}.t} \tag{2.1}$$

where, C_{out} and C_{in} are the outlet and inlet concentrations of the compound of interest (µg L^{-1}), Q is the flow rate of the enclosure purge air (L min^{-1}) and m_{dry} is the dried mass (g) of leaves or needles enclosed. Because the emission rate calculation depends directly on the difference in concentration between the outlet and inlet air, the procedure is greatly simplified if the inlet air is scrubbed and incoming BVOC concentrations can be considered negligible. The most common way to supply VOC-free air into the chambers is using inline scrubbers (generally filled with charcoal) (Hansen & Seufert, 2003; Holzke et al., 2006; Geron & Arnts, 2010) or zero air generators (Kim, 2001). Synthetic air cylinders (Harley, Guenther, & Zimmerman, 1995; Petron, Harley, Greenberg, & Guenther, 2001; Owen, Harley, Guenther, & Hewitt, 2002) were also used in related studies, but these bulky cylinders are difficult

to handle in field and may be impractical for large flow rates and even more CO_2 and H_2O may have to be added to achieve ambient level conditions. In some studies, the purge air was conditioned by passing flow through a heated (~300°C) palladium or Pt/Al_2O_3 catalyst systems (Komenda et al., 2001; Komenda & Koppmann 2002; Tani & Kawawata, 2008) which requires significant amounts of energy and causes excess heating of purge air. Consequently, inline scrubbers do not require heating or any other additions are advantageous for higher flow rates and field works.

BVOC concentrations in an enclosure may be very high soon after installation due to mechanical disturbances, then reduce in time (minutes to hours) to natural levels. Therefore, sampling of BVOCs right after the enclosing can cause non-realistic results so, samples should not be taken before steady-state conditions are reached inside the chamber. The time interval between installation and sampling is a variable that dependent on the volume of chamber and the flow rate of the purge air. According to these two factors, "equilibration times" are variable and they range from 35 min (Kim, 2001) to 24 h (Harrison et al., 2001) in the literature. However, because of isoprene is extremely volatile (reduces the analyte loses) and emission rates are much higher than the other VOCs, the equilibration-times were relatively short in isoprene-focused studies (Harley, Guenther, & Zimmerman, 1996; Padhy & Varshney, 2005). Equilibration time can be significantly shortened by smaller chamber volumes with higher purge flow-rates (Ortega & Helmig, 2008).

Enclosure materials should be selected with following considerations: no chemical contamination, inert surfaces, and transparency. Tedlar (polyvinyl fluoride) (Kim, 2001; Villanueva-Fierro et al., 2004; Baker & Sinnott 2009) and Teflon (fluorinated ethylene propylene, FEP) (Boissard et al., 2001; Harrison et al., 2001; Sabillon & Cremades, 2001; Holzke et al., 2006) films are the most frequently used materials for enclosures and glass vessels (Tani, Hayward, & Hewitta, 2003; Dominguez-Taylor et al., 2007) and polyvinyl chloride (PVC) (Arey, Crowley, Crowley, Resketo, & Lester, 1995) or polyethylene (PE) cuvettes (Tambunan et al., 2006) were also used as enclosure chambers in related studies.

Some examples for different enclosure materials were given in Figure 2.3. Other system components such as tubings, connection ports, internal parts of the air pumps and rotameters were also selected mostly Teflon or Teflon-coated (Helmig et al., 2004; Wilske et al., 2007; Raisanen, Ryyppo, & Kellomaki, 2009; Joo et al., 2010). Separately, in several studies enclosure systems were equipped with fans (Wilske et al., 2007; Baker & Sinnott, 2009; Joo et al., 2010) to increase the air circulation to ensure adequate mixing and uniform BVOC concentrations within the enclosures. A mixing fan will certainly help to distribute the air more uniformly, and will likely improve the homogeneity of air inside the enclosure, but operation of a fan adds complexity and weight to the enclosure experiment.

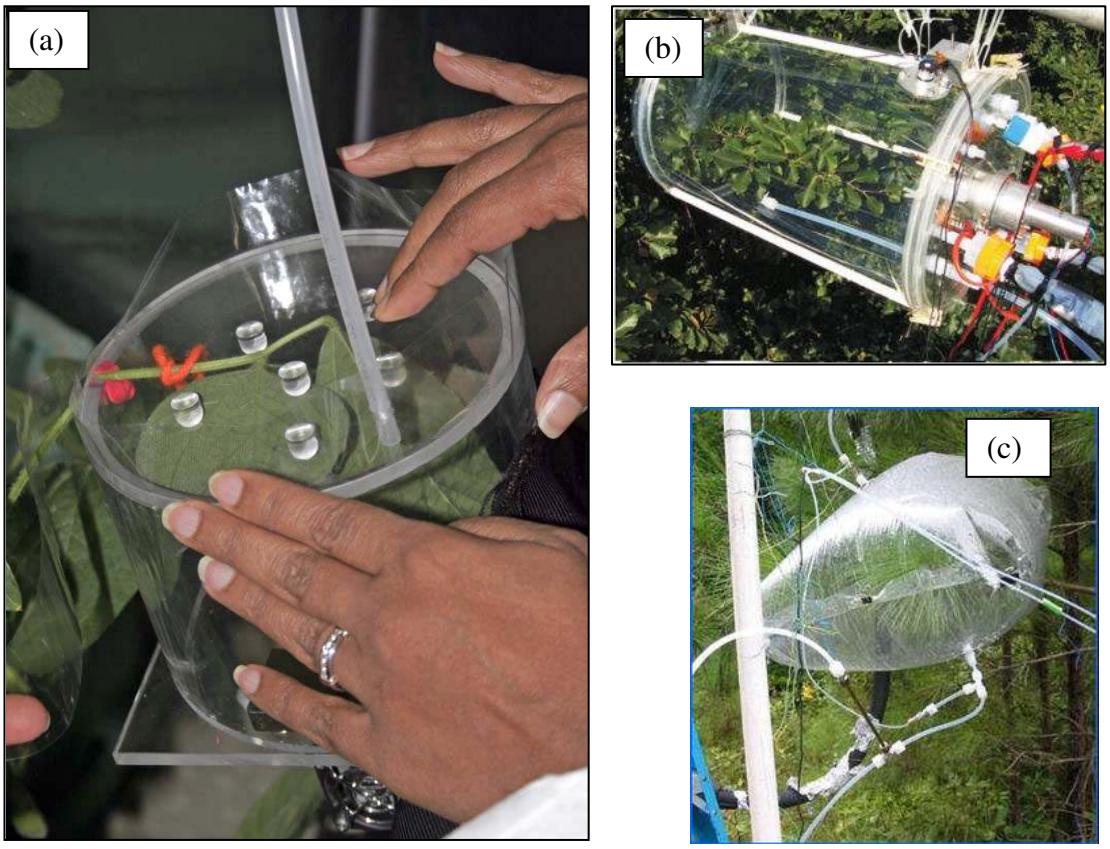

Figure 2.3 Enclosure chambers made of different materials a) Kuhn et al. (2002); b) Dindorf et al. (2006); c) Ortega et al. (2008).

Various sample collection and analysis techniques have been followed in related studies. On-site analysis or post-collection laboratory analysis are two primary pathways that have been used to quantify BVOC emissions from enclosure

experiments (see Figure 2.4). Reduction gas detectors (Harley, Guenther, Zimmerman, 1996; Geron, Guenther, Sharkey, & Arnst, 2000), argon ionization detectors (Sharkey, Singsaas, Vanderveer, & Geo, 1996), photoionization detectors (Keller & Lerdau, 1999) and chemiluminescence detectors (Guenther et al., 1996; Singsaas & Sharkey, 2000) were used particularly on-site isoprene emission studies. Many researchers used PTR-MS (Proton Transfer Reaction Mass Spectrometry) system in their studies (Karl et al., 2001; Tani, Hayward, & Hewitta, 2003; Graus et al., 2004; Steeghs et al., 2004). PTR-MS exhibits high time resolution and ability to monitor multiple compounds simultaneously in BVOC studies. However, compounds are identified according to their molecular masses, obtaining speciation for classes of compounds with the same molecular weight (e.g. monoterpene or sesquiterpene) is not possible (Ortega & Helmig, 2008). Furthermore, without enrichment or gas chromatographic (GC) separation, PTR-MS will typically not be as sensitive as what can be achieved with GC methods (Zhang & Li, 2010). BVOCs have been also sampled into electro-polished stainless steel canisters. Analysis of these whole air samples is commonly performed in the laboratory using cryo-focusing and GC-FID (Flame Ionization Detection) analysis (Kempf et al.,1996; Pressley et al., 2004). Solid adsorbent sampling followed by thermal desorption into a GC-FID or GC-MS (Mass Spectrometry) detection are two other techniques those are increasingly utilized in recent BVOC researches (Kim, Kim, Kim, Han, 2005; Pio, Silva, Cerqueira, & Nunes, 2005; Vuorinen, Nerg, Vapaavuori, & Holopainen, 2005; Hakola et al., 2006; Holzke et al., 2006; Helmig et al., 2007). These are established techniques for both compound identification and for quantification in the ppt to ppm concentration range. Porous organic polymers (e.g. Tenax TA, Tenax GR) (Pio et al. 2005; Vuorinen et al., 2005; Holzke et al., 2006; Helmig et al., 2007) and carbon-based materials (e.g. Carbotrap, Carbograph, Carboxen) (Steinbrecher, Hauff, Rabong, & Steinbrecher, 1997; Hakola et al., 2001; Dindorf et al., 2006) are the most frequently used solid-phase adsorbents.

Figure 2.4 BVOC measurements in field and laboratory (Copolovici & Niinemets, 2010; Baghi et al., 2012).

2.2.2 Other Measurement Methods

According to literature, BVOC studies which essentially focused on emission rates/ranges and/or species-specific emission factors, are mostly rely on leaf/branch/plant level enclosure methods and derivatives of those discussed above. Some plant species (e.g. grass, flowers and even some shrub and tree species) are not physically suitable for installing measurement instruments such as an enclosure chamber, thereby BVOC emissions from these species could not be investigated by these techniques. However, in several studies BVOCs investigated through canopy or landscape level measurements (Guenther et al., 1996; Karl et al., 2001; Bouvier-Brown, Goldstein, Gilman, Kuster, & de Gouw, 2009; Bamberger et al., 2010).

Tower-mounted micrometeorological techniques offer a means of measuring interactions between plant canopies and the atmosphere (see Figure 2.5). Temporally and spatially integrated estimates of the BVOC exchange occurring from the area upwind of the measurement point (flux footprint) can be well provided by applying this technique over homogenous plant canopies (Hewitt, Karl, Langford, Owen, &

Possell, 2011). Canopy level measurements are generally conducted over large scaled plot areas and so, they may be considered ideal for monitoring whole-ecosystem responses to environmental conditions. Fluxes of the BVOCs are calculated by combining co-located, high-frequency tower measurements of the vertical wind velocity and BVOC concentrations, and using Eddy Covariance (EC) method (Guenther et al., 1996; Karl et al., 2001; Greenberg et al., 2004, Spirig et al,. 2005; Langford, Davison, Nemitz, & Hewitt, 2009). Differently, some researchers investigated biogenic emissions at a constant height without considering vertical dispersion. Yassaa, Meklati, & Cecinato (2000) qualitatively and semi-quantitatively evaluated the BVOC emissions in ambient air around several trees from a height of about 3 m by following a basic active air sampling technique.

Figure 2.5 Sampling towers used in canopy level measurements (Steppe et al., 2009).

Various strategies have been deployed to characterize landscape level fluxes of BVOCs using airborne techniques. The most widely used method is the mixed layer budget (Greenberg et al., 1999). It requires knowledge about the lifetime of a BVOC species so the surface and entrainment fluxes can then be related to the lifetime of a compound and strongly depends on height of the planetary boundary layer (PBL). For instance, Greenberg et al. (2004) were used a tethered balloon-sampling platform to investigate BVOCs in the atmospheric boundary layer in tropical forest regions. More direct methods are based on the turbulent structure of the lower atmosphere and implemented by mixed layer gradient techniques. The mixed layer variance (MLV) method relates the variability (standard deviation) of a quantity (e.g. concentration) with its surface and entrainment fluxes. The MLV method has been successfully used to measure isoprene and monoterpene fluxes in Amazonia (Karl et al., 2007). Moreover, some researchers have followed "Eddy Covariance Method" by using measurement towers to determine the vertical diversity of plant based emissions (Guenther et al., 1996; Karl et al., 2001; Greenberg et al., 2004; Langford et al., 2009). Additionally, aircraft based observation techniques have been recently used in rare BVOC studies (Palmer et al., 2003; Palmer et al., 2006). Although at a very early stage of development, there is clearly considerable potential in these methods, and they may yield substantial progress in the next decade (Hewitt et al., 2011).

2.3 Previous Studies

2.3.1 Plant Species and Emissions

It is clearly recognized that vegetative emissions have a large inter-species and temporal/seasonal variability (Fall, 1999). It should also be noted that the reliability and the comparability of the reported values are biased by the diverse experimental conditions used in the studies. All these uncertainties canalized the recent studies to different measurement procedures that focusing on variables such as, species, season, plant tissues, measurement techniques, environmental conditions. The ambient conditions directly affecting biogenic emissions i.e., temperature, humidity, PAR, CO_2, are the most frequently investigated factors (Graus et al., 2004; Dindorf et al.,

2006; Monson et al., 2007). The age of the plants (Kim et al., 2005), biotic stress sources such as mites or caterpillars (Arimura, Huber, Bohlmann, 2004; Kant et al., 2004) and salt-stress (Loreto & Delfine, 2000) or elevated ambient O_3 concentrations (Vuorinen et al., 2005) as the abiotic stress sources are also discussed as effective parameters on emitting potential. Although most researchers conducted their measurements on living plants; cut branches, leaves or even root cultures were also analyzed in several studies (Helmig et al., 1999; Singsaas &Sharkey, 2000; Steeghs et al., 2004; Vuorinen et al., 2005). Monson et al. (2007) conducted measurements of isoprene emissions by using leaves attached to branches (50–70 cm long) that had been cut from the trees and immediately re-cut under water; the cut end of the branch was kept immersed in tap water during the gas-exchange measurements.

In order to understand biochemical emission mechanisms and related controlling factors in detail, long-term and one or a few species based studies can be more reasonable (Harley, Guenther, & Zimmerman, 1995; Kempf et al., 1996; Boissard et al., 2001; Geron & Arnts, 2010). Stone pine (*Pinus pinea*) and Scots pine (Pinus *sylvestris l.*) are two common trees, that were frequently examined for their seasonal and diurnal emission (especially monoterpenes) patterns (Staudt et al., 1997; Street, Owen, Duckham, Boisard, & Hewitt, 1997; Sabillon & Cremades 2001; Komenda & Koppmann, 2002; Raisanen, Ryyppo, & Kellomaki, 2009). Holzke et al., (2006) investigated diurnal and seasonal variation of terpene emissions from Scots pine to work out influences on atmospheric chemistry in different seasons for both mono- and sesquiterpenes. They carried out samplings for two years in different periods (monthly) by using two branches of different trees simultaneously. The effect of water stress on BVOC emissions of *Liquidambar styraciflua* was also surveyed by Fang, Monson, & Cowling (1996) with providing nine drying-rewatering cycles extending over five months. On the other hand, to determine species-specific emission factors/rates several species might be examined in the same study, varying from agricultural plants (rice, potato, cereal) to exotic decoration plants, flowering plants or even fruit trees (Owen et al., 1997; Drewitt, Curren, steyn, Gillespie, & Niki, 1998; Geron et al.,

2002; Padhy & Varshney 2005; Bao et al., 2008; Calfapietra, Fares, & Loreto, 2009; Dasdemir, Yaman, Elbir, & Odabasi, 2012). For instance, (Fares et al., 2011) measured the physiological parameters and BVOC emissions for four predominant *Citrus* species planted in California. Tambunan et al. (2006) screened 42 indigenous and exotic tropical trees in subtropic Okinawa, Japan for their isoprene emissions with triplicate measurements that were made for three leaves from three sample trees each (total 27 measurements for one species). Geron, Harley, & Guenther (2001) determined isoprene emission capacity for 18 American oak (*Quercus*) species and 6 species from other genera. As can be inferred from the literature, number of analyzed BVOCs were generally limited with experimental difficulties resulting from increasing number of plant species were examined in a study.

Getting knowledge on vegetative emissions of endemic species of a selected region may be very important to introduce the local BVOC profiles, hence they do not naturally grown in any other region and also may cause some specific indications in local air composition. Although, there are some studies aimed to screen the regional biogenic emissions by surveying the site-specific plants (Wilske et al., 2007; Bao et al., 2008; Calfapietra, Fares, & Loreto, 2009), most of the studies largely focused on common species as shown in Table 2.1 (Kempf et al., 1996; Boissard et al., 2001; Sabillon & Cremades 2001; Joo et al., 2010). In Japan, 42 indigenous species examined by Tambunan et al. (2006) for their isoprene emissions, included several endemic trees such as *Pinus luchuensis*, *Chamaecyparis obtusa* with determined isoprene emission rates of $0.1\pm0.0\ \mu g\ g^{-1}\ h^{-1}$ and $0.4\pm0.1\ \mu g\ g^{-1}\ h^{-1}$, respectively. *Cryptomeria japonica* and *Quercus myrsinaefolia* had total monoterpene and isoprene emissions of $2.81\ \mu g\ g^{-1}\ h^{-1}$ and $0.03\ \mu g\ g^{-1}\ h^{-1}$, respectively (Bao et al., 2008). Three native Mexican trees; *Abies religiosa*, *Quercus rugosa née* and *Pinus patula*, those all endemic to Mexico were also investigated for their isoprene and monoterpene emissions by Dominguez-Taylor et al. (2007) to guide the future biogenic emission inventories of the Mexico City area. Endemic plant species have been investigated in biogenic emission studies. While most of the researchers have studied on their target regions, to date there has been no study conducted on species specific emission factors or total biogenic emissions in Turkey.

Table 2.1 Previously reported BVOC emissions in µg g^{-1} h^{-1} for different tree species

Common Name	Genus / Species	Isoprene	MT	SQ	OX	Distrubution Region	Ref.
Coniferous Species							
Stone Pine	*Pinus pinea*	n.d.	7.38±4.90	n.r.	n.r.	Mediterranean Region	1
		n.r.	6.50±5.40	n.r.	n.r.		2
		n.r.	7.00 - 15.00	n.r.	n.r.		3
		0.084±0.062	1.11±0.84	0.0065±0.0044	2.20±1.37		4
Scots Pine	*Pinus sylvestris*	n.r.	3.80±0.80	n.r.	n.r.	North of Europe and Asia	5
		n.r.	0.06 - 3.70	n.r.	n.r.		6
		0.18±0.098	1.57±0.66	0.027±0.023	0.73±0.33		4
Norway Spruce	*Picea abies*	0.34	3.15	n.r.	n.r.	Europe	7
		0.01±0.01	n.r.	n.r.	n.r.		8
Loblolly Pine	*Pinus tadea*	n.r.	4.36±4.00	0.36±0.24	0.20±0.26	Southeastern U.S.	9
Virginia Pine	*Pinus virginiana*	n.r.	1.98±1.05	1.84±1.15	<0.01	Southern U.S.	9
Japanese Cypress	*Chamaecyparis obtusa*	0.40±0.10	n.r.	n.r.	n.r.	Japan	10
Luchu Pine	*Pinus luchuensis*	0.10±0.00	n.r.	n.r.	n.r.	Japan	10

Table 2.1 Continued

Broad-Leaved Species							
American Sweetgum	*Liquidambar styraciflua*	29.0±16.5	n.r.	n.r.	n.r.	North and Central America	11
		68	n.r.	n.r.	n.r.		12
American Sycamore	*Platanus occidentalis*	27.5	n.r.	n.r.	n.r.	North America	13
		71	n.r.	n.r.	n.r.		12
Black Locust	*Robinia pseudoacacia*	151	n.r.	n.r.	n.r.	N. America, S. Africa,Europe, Asia	12
		12.4±11.1	0.075±0.031	0.013±0.0061	0.041±0.031		4
Aspen Poplar	*Populus tremula*	13.6	0.73	n.r.	n.r.	Many parts of Asia and Europe	14
		22.4±11.2	0.23±0.18	0.015±0.012	0.034±0.018		4
Cottonwood Poplar	*Populus deltoides*	7.57±9.26	0.15±0.12	0.032±0.036	0.038±0.020	S.E. and Central U.S.	4
Blue Gum	*Eucalyptus globulus*	9.90±4.80	n.r.	n.r.	n.r.	S. Europe, S. Africa	15
River Red Gum	*Eucalyptus camaldulensis*	5.14±4.04	0.17±0.17	0.078±0.089	0.41±0.53	World wide	4
Willow	*Salix phylicifolia*	50.2	0.42	n.r.	n.r.	Northern Europe	14

n.r.: not reported, n.d.: not detected, MT: monoterpenes, SQ: sesqiterpenes, OX: oxygenated compounds. "±" refers the values with standard deviations (value±std. dev.). "-" refers the values in intervals. References: [1]: (Street et al., 1997), [2]: (Sabillon a& Cremades, 2001), [3]: (Staudt et al., 1997), [4]: (Elbir et al., 2013), [5]: (Raisanen, Ryyppo, & Kellomaki, 2009), [6]: (Komenda & Koppmann, 2002), [7]: (Kempf et al., 1996), [8]: (Isebrands et al., 1999), [9]: (Geron & Arnts, 2010), [10]: (Tambunan et al. 2006), [11]: (Harley, Guenther, & Zimmermann, 1996), [12]: (Geron, Harley, & Guenther, 2001), [13]: (Evans, Tingey, Gumpertz, & Burns, 1982), [14]: (Hakola, Rinne, & Laurila, 1998),[15]: (Padhy & Varshney, 2005).

2.3.2 Estimation of Emissions

Estimation of BVOC emissions is a multi-disciplinary research topic, that involves knowledge in botanical science, scientific computing, atmospheric science, and geography (Leung, Wong, Cheung, & Guenther, 2010). Given above the important roles of BVOCs in determining atmospheric chemistry, it is essential to accurately estimate their concentrations for the atmospheric photochemical modeling purposes (Zemankova & Brechler, 2010). Estimation and inventorying studies can be considered as the data processing stages after plant or canopy level BVOC measurements and largely conducted for the investigation of the effects of biogenic emissions on the air pollution.

Computer based BVOC emission models are useful tools for estimating BVOC emission inventories and they have been applied to many regions in the world (Scott & Benjamin 2003; Parra, Gasso, & Baldasano, 2004; Sakulyanontvittaya et al., 2008; Leung et al., 2010). An accurate modeling approach requires three basic datasets. The first is a land use dataset, with specific spatial and land use category resolution. The dataset is compiled on the basis of survey/census data/satellite observations, or a combination of these (Kinnee, Geron, & Pierce, 1997). The second is a set of emission factors, associated with each of the land use categories under certain ambient conditions (Lamb et al. 1987; Guenther et al., 1996), and the third is a set of algorithms to account for environmental corrections due to meteorological parameters (Geron et al., 2000). Thereby, researchers could adapt the models for data of the interested region and generate the local or global patterns of biogenic emissions, since models can include some default variables which may not be similar to interested regions'.

In United States, the EPA BEIS3.0 (Environmental Protection Agency Biogenic Emissions Inventory System 3) (http://www.epa.gov/asmdnerl/biogen.html) is the most commonly used biogenic emissions model, that includes isoprene, monoterpenes and many other species. BEIS was first developed in 1991 (Pierce & Waldruff ,1991), and updated in the

late 1990s to BEIS2 (Pierce et al., 1998). The two latest versions; BEIS3.12 and BEIS3.13 include a 1 km x 1 km vegetation database that resolves forest canopy coverage by tree species, and emission factors for 34 chemicals including isoprene, 14 monoterpenes and methanol. BEIS models are also integrated with Sparse Matrix Operator Kernel Emissions (SMOKE) processor as a part of EPA's Community Multiscale Air Quality (CMAQ) modeling system. Yin, Jiang, Roth, & Giroux (2004) modified the land use dataset, emission factors and model algorithms of the BEIS2.0 and implemented it in the SMOKE processors in an effort to reduce modeling uncertainties, and to give better biogenic emissions estimation and better source contribution assessment for the Lower Fraser Valley region. Additionally, Chang, Chen, & Huang (2005) customized BEIS2.0 to The Taiwan Biogenic Emission Inventory System (TBEIS) with following some fittings on the empirical coefficients used in the BEIS2.0. GloBEIS (The Global Biogenic Emission Inventory System) is additionally a BEIS based model which developed by Guenther et al. (1999) and then used to compute annual emissions of isoprene, monoterpenes, and other VOCs from North America (Guenther, Geron et al. 2000). Symeonidis et al. (2008) developed a system for estimating biogenic non-methane VOCs emissions based on the GloBEIS model and used this to estimate the biogenic emissions from the Balkan Peninsula in Europe. Song et al. (2008), compared modeled results from GloBEIS with observed isoprene concentrations from ground and aircraft measurements in southeast Texas and found good agreement for diurnal isoprene patterns.

Another model, recently introduced by Guenther et al. (2006), is called MEGAN2 (Model of Emissions of Gases and Aerosols from Nature, version 2), which is a detailed global model for isoprene and more than 100 other VOCs. MEGAN2 is publicly available at http://cdp.ucar.edu. It is a global-scale model with a base resolution of ~1 km^2 (30 s latitude by 30 s longitude) to enable both regional and global model simulations (Warneke et al., 2010). MEGAN has been applied to many studies including the estimation of emissions and OH reaction potential of BVOCs from a mixed northern hard-wood forest. MEGAN has been used to estimate both branch-level emissions of individual tree species and whole-canopy fluxes of

isoprene, monoterpenes, and sesquiterpenes at specific locations (Ortega et al., 2007) and regional to global scale studies (Heald et al., 2009). Recently, Sakulyanontvittaya et al. (2008) used MEGAN version 2.02 to estimate emissions of BVOCs across the United States with a focus on monoterpenes and sesquiterpenes in particular. Some emission factors are provided in their paper based on recent laboratory measurements. When compared to the BEIS3.0, MEGAN was found to estimate higher isoprene but lower monoterpene emissions for the period between July 2001 and January 2002 (Sakulyanontvittaya et al., 2008). A comprehensive study was also conducted by Warneke et al. (2010) that four models [BEIS3.12, BEIS3.13, MEGAN2, and WM2001 (developed by Wiedinmyer et al. (2001) only for Texas)] were used to evaluate the results of four major emission measurement campaigns: Southern Oxidant Study 1999 (SOS1999), Texas Air Quality Study 2000 (TexAQS2000), International Consortium for Atmospheric Research on Transport and Transformation (ICARTT2004), and Texas Air Quality Study 2006 (TexAQS2006).

CHAPTER THREE
MATERIALS AND METHODS

Endemic tree species in Turkey, sampling program, sampling methods, laboratory analysis, quality control/quality assurance and calculation of BVOC emission factors are explained in this chapter.

3.1 Endemic Tree Species in Turkey

Seven endemic tree species consisting of three coniferous and four broad-leaved trees were investigated. The coniferous species were composed of firs (*Abies*) which is a difficult genus with several problems in its taxonomy (Bagci, Baser, Kurkcuoglu, Babac, & Celik, 1999). Turkey has four of the forty fir species known in the world which covers 2136 km^2 land area as pure fir forestlands, and three of these (Troy Fir, Cilician Fir, Uludag Fir) are endemics that were investigated in this study (GDF, 2010). The four broad-leaved species included three oaks and a sweetgum species. Oriental Sweetgum (or Turkish Sweetgum) is a rare endemic tree such that has a narrow distribution only about 5 km^2, additionally it has a special oiled secretion (balsam or sweetgum oil) that is used as a medicinal product like the other sweetgum species (Celik, Guvensen, Secmen, & Ozturk, 1997; GDF, 2010). Oak (*Quercus*) species have the largest natural reserve in Turkey's forestland inventory including 18 species, 9 subspecies, 2 varieties and 7 natural hybrids (GDF, 2004). Further information for the studied species is given below:

1. Troy Fir (*Abies nordmanniana* subsp. *equi-trojani*) is naturally grown in Ida-Mountains, Canakkale, Turkey. It can form pure or mixed stands and settles 400 to 1650 meters altitude in a limited area about 3600 ha (Ata, 1989; Kaya, Skaggs, & Neale, 2008). Troy Fir has proven to be resistant to drought and heat in summer and over winter frost and grow up to between 22 and 30 meters height and 40 to 65 cm diameter of trunk.

2. Boz Pirnal Oak (*Quercus aucheri*) is an oak species of Turkey which is endangered and listed as "lower risk/near threatened" by International Union for Conservation of Nature (IUCN, 1998). The tree can grow up to a height of maximum 5-6 meters and naturally grown in southwestern of Turkey (Antalya, Aydin, Mugla). It is an evergreen tree and prefers mild temperate zones, warmer summers and sunlight. It could grown in a good deep fertile loam that can be on the stiff side and tolerates reasonable amounts of lime in dry soils (Hedge & Yaltirik, 1982)

3. Oriental Sweetgum (*Liquidambar orientalis*) has a local distribution in the south-western coastal district of Turkey (Koycegiz, Fethiye, Marmaris and Milas). Although the congenerous species can occur 0 to 1800 meters altitudes, Oriental Sweetgum mostly grown under maritime conditions with sandy and humid soils with a height of about 20-25 meters (Efe, 1987; Ickert-Bond, Pigg, & Wen, 2005).

4. Cilician Fir (*Abies cilicica* subsp. *isaurica*) is a narrowly pyramidal tree 25-35 m tall, to 210 cm in girth, with ascending branches. Two subspecies of Cilician Fir grown in Turkey: *Abies cilicica* subsp. *cilicica* and the endemic one which was investigated in this study, *Abies cilicica* subsp. *Isaurica.* It mostly occurs in the south of Turkey, Taurus Mountains at the altitudes from 1000 to 2100 meters (Boydak & Erdogrul, 1999).

5. Uludag Fir (*Abies nordmanniana* subsp. *bornmuelleriana*) has a distribution that covers the Black Sea region from the west of Kizilirmak River to Mount Uludag and from sea level to 2000 m altitude. Like all the other firs, Uludag fir is also grown in regions with high precipitation (above 1000 mm rainfall), it is an evergreen, semi-shade and sun tree (Ozturk & Guvenc, 2010).

6. Ispir Oak (*Quercus macranthera* subsp. *syspirensis*) can grow up to 7 m height at between 1000-1900 m above sea level on dry slopes. In general, this taxon lives in northern part of Anatolia, in provinces of Bolu, Zonguldak, Bartin, Karabuk, Kastamonu, Yozgat, Corum, Amasya, Sivas, Gumushane, Erzincan,

Bayburt, Erzurum and Kars. Ispir Oak is a non-evergreen tree and prefers to grow in slightly alkaline, non-calcareous brown forest or non-calcareous brown soils (Kargioglu, Serteser, Senkul, & Konuk, 2011).

7. Vulcanic Oak (*Quercus vulcanica*) as named by the natives, occupies an area over 8000 ha's near the province of Isparta in southern Turkey (Balaban, Yilgor, & Strobel, 1999). Vulcanic Oak also occurs in Sultan Mountains and Karadag-Karaman at 1350 to 2000 m altitudes with limestone bedrock. The tree can reach up to 27 m in height, its trunk could be 140 cm in diameter and it can achieve the age of 600 years (Kargioglu, Senkul, Serteser, & Konuk, 2009).

3.2 Sampling Program

On-site measurements were conducted in the natural habitats of seven tree species between June 2011-August 2012. Three middle-aged (20-40 years) and healthy (i.e., no pest or aphid affected, having well-developed stem and branches, not obstructed by neighboring plants, favorable soil conditions and no other biotic/abiotic stress sources) trees were selected for sampling to produce the average BVOC emission factors. BVOC samples were collected simultaneously from two different branches of three selected trees of each species. Thus, BVOC emission rates of each species were calculated by averaging six values (3 trees x 2 branches). Measurements were conducted during normal metabolic activities of trees under the presence of sunlight (generally between 10:00 a.m. - 14:00 p.m.) in summer months. All sampled trees were selected in open parts of the forest canopy to avoid underestimation of emissions due to the shaded leaves during sampling. The collected samples were kept at 4°C until they were analyzed in the laboratory. Table 3.1 illustrates the sampling program in detail and the study sites are also given in Figure 3.1.

Table 3.1 Sampling program and environmental parameters during the samplings

Species	**Sampling Date**	**Region**	**Coordinates (UTM)**	**Averaged Environmental Parameters During the Samplings**							
				Ambient air				**Inside the enclosure chamber**			
				T (°C)	**RH (%)**	**PAR (µmol/m^2 s)**	**CO_2 (ppm)**	**T (°C)**	**RH (%)**	**PAR (µmol m^2 s)**	**CO_2 (ppm)**
Troy Fir	08-10.07.2011	Mount Ida /Canakkale	(35N) 510030, 4395705	24.8	45.7	1756	367	34.7	32.1	1580	425
Boz Pirnal Oak	23-25.07.2011	Gumbet-Bodrum/Mugla	(35N) 538885, 4105584	35.7	29.6	1707	370	42.3	34.1	1536	376
Oriental Sweetgum	27-29.07.2011	Koycegiz/Mugla	(35N) 652300, 4085250	34.8	46.1	1747	369	43.7	36.3	1573	287
Cilician Fir	09-11.09.2011	Dagpazari-Mut/Mersin	(36N) 547660, 4070820	24.4	34	1691	367	30.4	11.2	1522	339
Uludag Fir	20-22.06.2012	Aladag/Bolu	(36N) 381554, 4497233	22.7	45	1894	397	31.6	25.6	1705	378
Ispir Oak	18-20.07.2012	Mudurnu/Bolu	(36N) 353189, 4494034	26.6	51.1	1502	389	30.1	35.8	1352	268
Vulcanic Oak	06-08.08.2012	Egirdir/Isparta	(36N) 309013, 4178771	26.3	38.6	1073	401	30.2	33.9	965	275

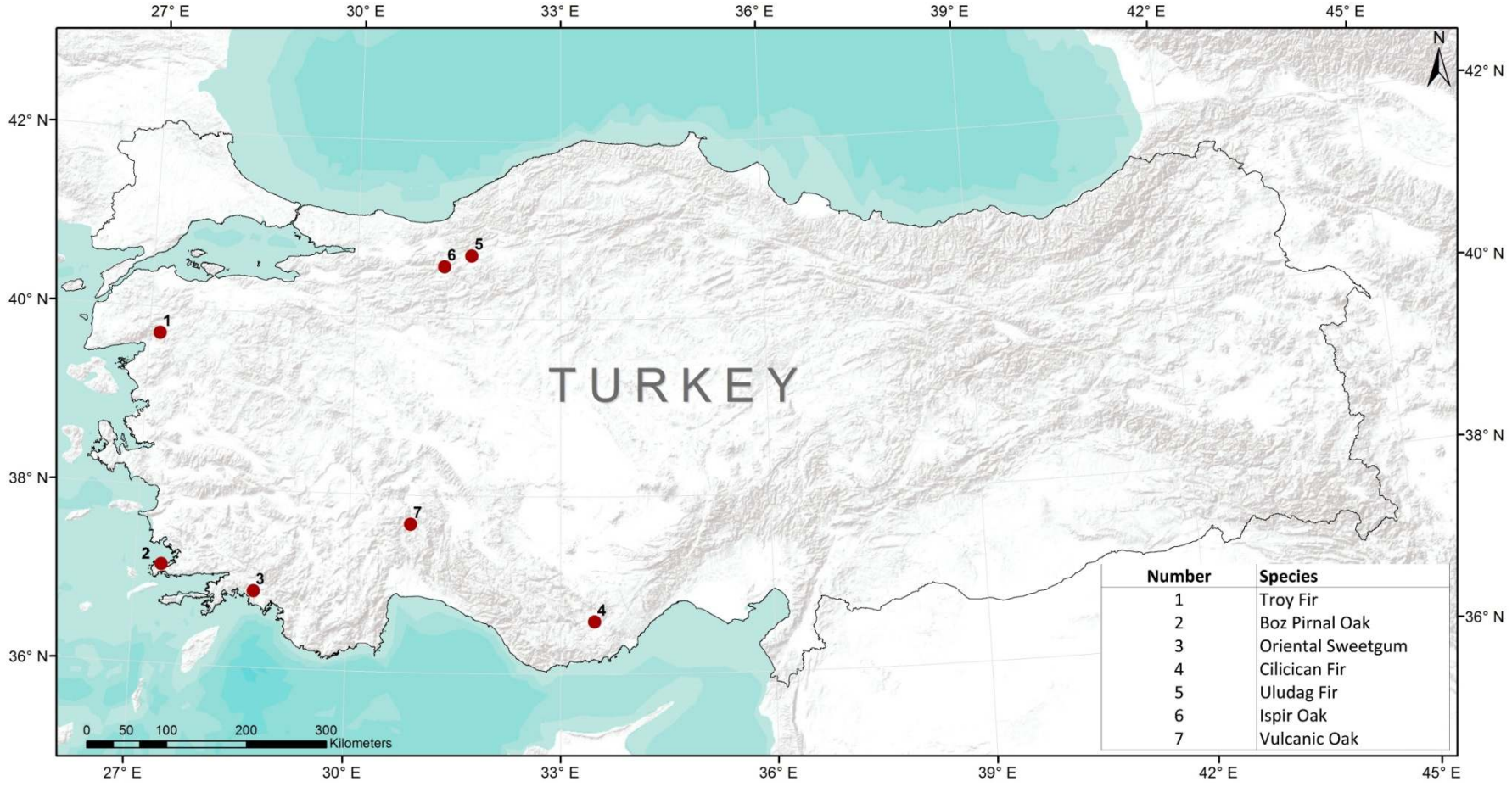

Figure 3.1 Sampling sites.

3.3 Sampling Method

A specialized dynamic branch enclosure system was used within the study. Selected healthy branches of the trees were enclosed into transparent Nalofan bags (with a volume of approximately 7 L [see Figure 3.2]) and air composition in bags were sampled with Tenax-filled adsorbent tubes. Temperature, humidity, CO_2 concentration and PAR were concurrently monitored and recorded in ambient air and in the enclosure. Conditions in the enclosure were regulated to provide similar conditions to ambient air. Air circulation of the enclosure was provided by consistent air inflow and outflows via Teflon tubings on the line of diaphragm pumps (Rocker 300). The inflow air was conditioned by passing through three sequential columns containing silica gel, potassium iodide (KI) and activated carbon. Schematic description of the sampling system used in this study is given in Figure 3.3. Both purified inflow and BVOC contained outflow rates were regulated/measured by automatic mass flow controllers (MFCs) (Aalborg DFC26) at 350 and 9 L h^{-1} respectively. There were also two other Teflon tubes placed in the enclosure for by-passing the excess air and supplying air to the CO_2 analyzer (Li-Cor LI-840A) at a flow-rate of 1 L h^{-1}. The auxiliary equipments used in the study were shown in Figure 3.4. Under sunlight, greenhouse effect causes increasing temperatures resulting in deviation from ambient conditions. In order to avoid this problem, cold water provided by a circulating water bath was circulated by a spiral Teflon tubing inside the bag. The humidity/temperature probe inside the chamber (T&D Thermo Recorder TR-77Ui) was also placed in a small cone-shaped case to protect it from direct sunlight. The use of PAR probe (Li-Cor LI-190 Quantum Sensor) requires placing its sensor on a planar surface. Therefore, the PAR measurements were performed outside of the enclosure (on a ground-level) and the inner values were corrected based on an experimentally derived constant ratio (~10% net loss). Additionally, all the components of the measurement system including air conditioning columns, inertness of the Nalofan bags and Teflon tubings, pumps and the auxiliary equipments was tested both on-site and in laboratory during the preparation processes.

Figure 3.2 Enclosure chambers used in this study.

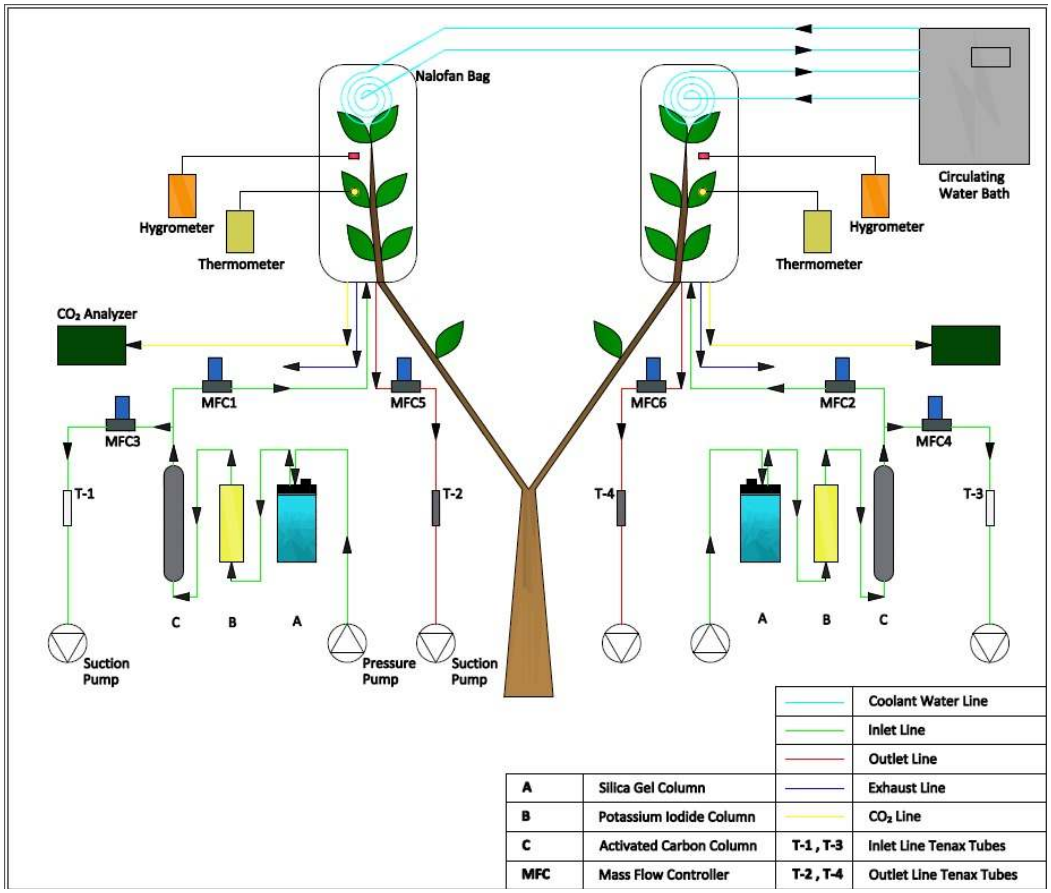

Figure 3.3 Operational scheme of the measurement system.

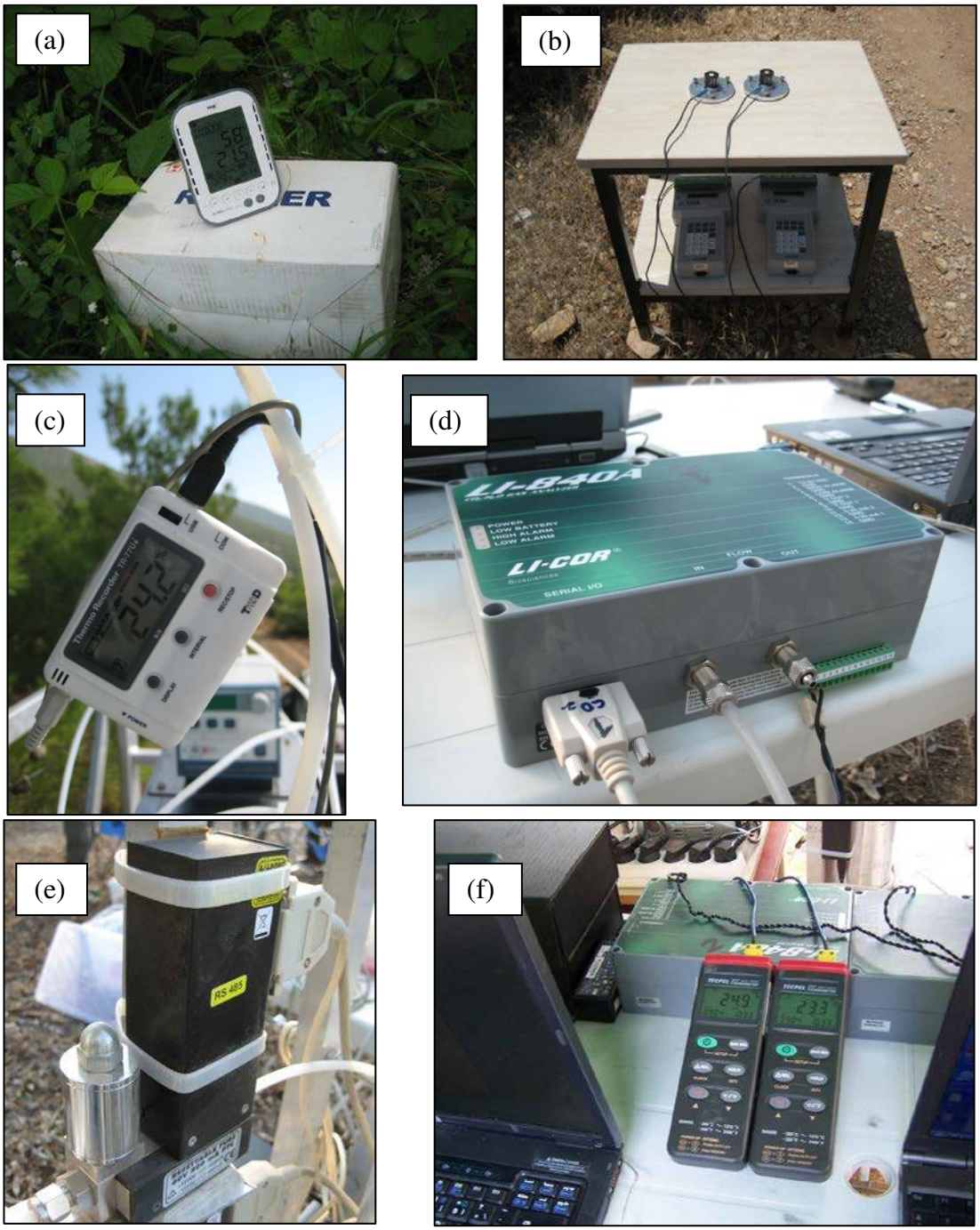

Figure 3.4 Auxiliary equipments; (a) Ambient air thermometer, (b) PAR measurement devices, (c) inside-chamber thermometer, (d) CO_2 measurement device, (e) mass flow controller (MFC), (f) leaf temperature measurement devices.

Installation of the enclosure chamber was the most critical operation of the sampling which should be achieved without any damage to branches and leaves since this may cause overestimated monoterpene emissions. For the first two hours of experiment, enclosure system was purged with purified ambient air to

provide steady-state environmental conditions and stabilize the emissions from possible initial disturbances during installation of the chamber. The purge time was selected as 2 h based on a recent study indicating that emissions are stabilized within this period (Oz, 2012). Following the purging, the air was sampled simultaneously from both the inlet and outlet ports for an hour. Tenax TA filled sorbent tubes were used to adsorb BVOCs. At the end of the sampling the sorbent tubes were placed into their containers and stored at -20°C until they were analyzed (see Figure 3.5). The leaves from the enclosed branches were only collected and total weight (with Ohaus CT600-S analytical balance) and leaf area (with Li-Cor LI-3000C portable area-meter) of the collected foliage were measured after sampling (see Figure 3.6). Dry weight was determined by oven-drying (with Nüve FN 055 oven) of the leaves for two days at 60°C. Using these data, both dry foliage weight and leaf area based emission factors were calculated.

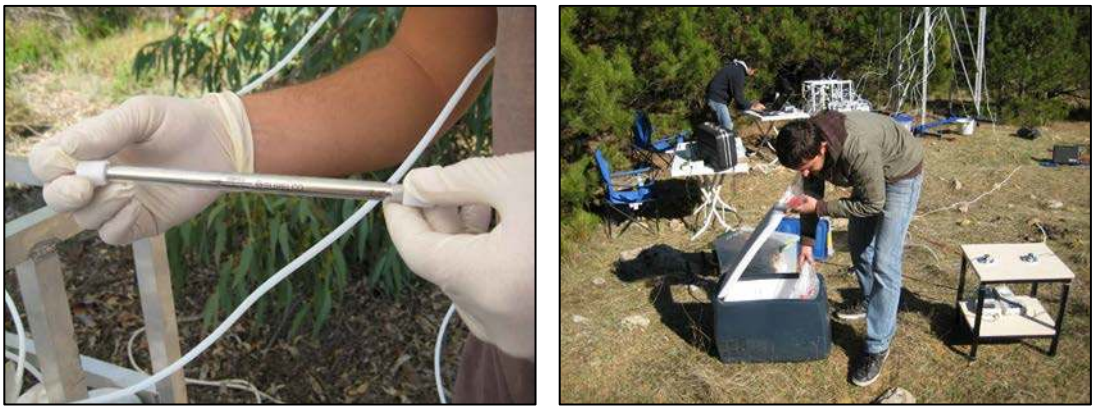

Figure 3.5 Tenax-filled sorbent tubes.

Figure 3.6 Measuring enclosed leaf area and foliage weight.

Dynamic branch enclosure method was simultaneously applied to two different branches of each tree with a pair of identical measurement systems. Thus, the emission rates for each BVOC were calculated by averaging six measurements (3 trees x 2 branches).

Figure 3.7 General view of the system during the measurements.

3.4 Laboratory Analysis

Before sampling, Tenax-filled sorbent tubes were conditioned with a 40 mL min^{-1} flow of helium at 240°C for 10 minutes and they were kept in their containers containing silica gel and activated carbon until they were used for sampling.

Samples were analyzed for 65 compounds (isoprene, 21 monoterpenes, 15 sequiterpenes, 3 oxygenated sesquiterpenes, and 25 oxygenated VOCs) with a gas chromatograph (GC) (Agilent 6890N, Agilent, Wilmington, DE, USA) equipped with a mass selective detector (Agilent 5973 inert MSD, Agilent, Wilmington, DE, USA) and a thermal desorber (Tekmar, Aerotrap 6000, USA). Samples were desorbed for 10 min at 240°C using helium flow at the rate of 40 mL min^{-1}. Internal trap temperature during sample desorption was 35°C. The trap was desorbed for 1 min at 240°C. Then, it was baked for 10 min at 250°C. Valve oven and transfer line temperature of the thermal desorber was 200°C.

The chromatographic column was HP5-MS (30 m, 0.25 mm, 0.25 µm) and the carrier gas was helium at 1 mL min^{-1} flowrate and 37 cm s^{-1} linear velocity. The split ratio was 1:40. The inlet temperature was 240°C. Temperature program for VOCs was: initial oven temperature 40°C, hold 3 min, 40°C to 120°C at 5°C min^{-1}, hold 5 min, 120°C to 240°C at 30°C min^{-1}, hold 3 min. Ionization mode of the MS was electron impact (EI). Ion source, quadrupole, and GC/MSD interface temperatures were 230, 150, and 280°C, respectively. GC/MS was operated at "scan" and "selected ion monitoring" modes simultaneously. Compounds were identified based on their retention times (within ±0.05 minutes of the retention time of calibration standard), target and qualifier ions and were quantified using the external standard calibration procedure.

Six levels of VOC solutions were prepared in methanol as the calibration standards. Thermal desorption tubes used for calibration were loaded by spiking with 1 µl of the calibration standards (Odabasi, Ongan, & Cetin, 2005; Dincer, Odabasi, & Muezzinoglu, 2006). Then, the standard loaded tubes were run at specified

conditions to calibrate the analytical system (Thermal desorber-GC-MS). In all cases linear fit was good with r^2>0.999.

3.5 Quality Assurance/Quality Control

Instrumental detection limits (IDL) were determined from linear extrapolation, based on the lowest standard in calibration curve and using the area of a peak having a signal/noise ratio of 3. The quantifiable VOC amounts were between 5.7 (p-cymene) and 295 pg (guaiol). Blank Tenax tubes were routinely placed in the field to determine if there was any contamination during sample handling and preparation. The limit of detection of the method (LOD, pg) was defined as the mean blank mass plus three standard deviations. Instrumental detection limit was used for the compounds that were not detected in blanks. LOD ranged between 7.5 (trans-dihydro-b-terpineol)-1455 (crotonaldehyde) pg. Average VOC amounts in blanks were 5% of the amounts found in samples. Samples were blank-corrected by subtracting the average blank amount from the sample amount. Using an average sampling volume of 0.009 m^3, limit of detection of the method ranged between 0.0008 (trans-dihydro-b-terpineol) and 0.16 (crotonaldehyde) $\mu g\ m^{-3}$.

The system performance was confirmed daily by analyzing a midrange calibration standard. If the relative standard deviation from the initial calibration was <10%, system was recalibrated. Analytical precision determined from three pairs of duplicate samples ranged between 2-5%.

Inlet concentrations of the chamber were close to blank concentrations indicating that activated carbon trap effectively removed the BVOCs from purge air. Use of the cold water circulation kept the temperature difference between the ambient air and bag within 5°C. Net photosynthesis rates during the samplings were also calculated using the leaf area, inlet and outlet CO_2 concentrations, and purge flow rate. Average rates ranged between –1110 and 27600 $\mu mol\ CO_2\ m^{-2}\ h^{-}$

[1], indicating that photosynthesis was the dominant mechanism rather than respiration during the samplings.

3.6 Calculation of BVOC Emission Factors

In this study, emission factors (ε, μg compound g^{-1} h^{-1}) of the investigated BVOCs were determined by measured BVOC concentrations, gas flow-rates, sampling time and dry weight of the sampled foliage as given in Equation (3.1) (Ortega et al., 2008).

$$\varepsilon = \frac{(C_{outlet} - C_{inlet}).Q.t}{m.t} \tag{3.1}$$

where, C_{outlet} and C_{inlet} are the concentrations (μg m^{-3}) measured at outlet and inlet of the enclosure bag, respectively; Q is the air flow-rate (m^3 h^{-1}) pumped to the bag; t is the sampling time (h), m is the dry weight (g) of the enclosed foliage.

The emission factors were normalized to standard conditions (30°C and 1000 μmol m^{-2} sec^{-1} PAR). The emission rates under standard conditions are called species specific emission factors (IEF) (Pacifico, Harrison, Jones, & Sitch, 2009).

Amount of monoterpenes was calculated depending on the ambient temperature using the equation (Guenther, Zimmerman, Harley, Monson, & Fall, 1993):

$$\varepsilon_{mtp} = \varepsilon_{mtps}\, \gamma_{mtp} \tag{3.2}$$

$$\gamma_{mtp} = exp\, \beta\, (T - T_s) \tag{3.3}$$

where, ε_{mtp} is emission factor for monoterpenes, ε_{mtps} is emission factor under standard conditions (30°C and 1000 μmol m^{-2} sec^{-1} PAR), T is the ambient temperature (K), T_s is the temperature at normal conditions (303 K), β is the empirical constant (0.09 K^{-1}) and γ_{mtp} is the correction factor.

Guenther et al. (1993) have developed a different algorithm to calculate isoprene rates that are related with temperature and light intensity. Isoprene emission rates at

any temperature and PAR are determined by multiplying measured emission rate (ε_s) with temperature (C_T) and light (C_L) correction factors.

$$\varepsilon_{iso} = \varepsilon_{isos} C_L C_T \quad (3.4)$$

$$\gamma_{iso} = C_L C_T \quad (3.5)$$

where, ε_{iso} is the emission factor for isoprene, ε_{isos} is the emission factor under standard conditions, C_T and C_L are the temperature and light related coefficients, respectively, and γ_{iso} is the correction factor.

According to emission measurements, light (C_L) (Guenther et al., 1993) and temperature (C_T) (Dominguez-Taylor et al., 2007) based correction factors were formulated as:

$$C_L = \frac{\alpha C_{L1} L}{\sqrt{(1 + \alpha^2 L^2)}} \quad (3.6)$$

where, C_{L1} (1.066) and α (0.027) are the empirical constants, L is the PAR value (μmol m^{-2} s^{-1}).

$$C_T = \frac{exp C_{T1}(T - T_S)/\, RT_S T}{1 + exp C_{T2}(T - T_M)/\, RT_S T} \quad (3.7)$$

where, T is the ambient temperature (K), R is the ideal gas constant (8.134 J K^{-1} mol^{-1}), T_S is the temperature under standard conditions (303 K), TM (314 K), C_{T1} (95 000 J mol^{-1}) and C_{T2} (230 000 J mol^{-1}) are the empirical constants.

The emission factors measured at different environmental conditions were calculated according to Equation (1) and they were corrected for standard conditions [i.e., monoterpenes and other BVOCs were normalized using the Equations (3.2), (3.3), and isoprene was calculated using equations (3.4), (3.5), (3.6), and (3.7)].

CHAPTER FOUR
RESULTS AND DISCUSSION

This chapter presents the results of total BVOC emissions and their characterization. Findings were also discussed and compared with the literature.

4.1 Total BVOC Emissions

Emission factors for 65 analyzed BVOCs were calculated. Table 4.1 summarizes the average emission factors of 65 BVOCs for seven endemic tree species in Turkey. Categorized emission factors into five basic groups (isoprene, monoterpenes, sesquiterpenes, oxygenated sesquiterpenes and oxygenated compounds) in both $\mu g\ g^{-1}\ h^{-1}$ and $\mu g\ m^{-2}\ h^{-1}$ were also given in Table 4.2 and in the appendices Table A.1, respectively. Additionally the raw emission factors under experimental conditions were also given in Appendices B.

On the basis of total emissions, Ispir Oak, Oriental Sweetgum and Cilician Fir were the top three BVOC emitters with the total emission factors of 19.4±19.1, 16.5±16.3 and 15.5±11.5 $\mu g\ g^{-1}\ h^{-1}$, respectively while Boz Pirnal Oak had the lowest emission rate of 0.94±0.74 $\mu g\ g^{-1}\ h^{-1}$. Isoprene was the prominent compound for Cilician Fir, Vulcanic Oak, Ispir Oak and Oriental Sweetgum while the others were mainly monoterpene emitters (Figure 4.1). For these isoprene emitter species, it consisted of more than 90% of the total emissions. Monoterpenes dominated the emissions of Boz Pirnal Oak, Troy Fir, and Uludag Fir. Boz Pirnal Oak had the highest monoterpene ratio of 92.9% and Uludag Fir had the highest quantity of $2.30 \pm 1.28\ \mu g\ g^{-1}\ h^{-1}$. On the other hand, sesquiterpenes were a relatively less significant BVOC group as they contributed less than 0.8% to total emissions of each tree species. Oxygenated compounds had higher percentages than sesquiterpenes for all tree species and even than isoprene for Boz Pirnal Oak. Furthermore, 15.5 and 11.6% of all emissions consisted of oxygenated compounds for Troy Fir and Uludag Fir, respectively.

Table 4.1 BVOC emission factors (average±standard deviation) for the trees (µg g^{-1} h^{-1}) at standard conditions (at 1000 µmol m^{-2} s^{-1} and 30°C)

Group	Compound	Troy Fir	Cilician Fir	Uludag Fir	Boz Pirnal Oak	Ispir Oak	Vulcanic Oak	Oriental Sweetgum
Isoprene	**Isoprene**	**1.34±1.11**	**14.1±10.5**	**1.50±1.39**	**0.028±0.026**	**19.2±19.0**	**9.79±7.57**	**15.0±15.2**
MT	Tricyclene	0.0048±0.0045	0.00046±0.00021	0.0015±0.00098	0.00051±0.00079	0.00047±0.0004	0.00025±0.00028	0.00014±0.000051
MT	Alpha-Pinene	0.18±0.070	0.41±0.32	1.44±0.96	0.014±0.00049	0.016±0.020	0.02±0.017	0.049±0.046
MT	Alpha-Fenchene	0.0029±0.0031	0.00044±0.00023	0.00049±0.00022	0.00019±0.000073	n.d.	n.d.	0.00016±0.000030
MT	Camphene	0.036±0.020	0.0025±0.0016	0.023±0.012	0.00066±0.00058	0.0017±0.0012	0.0012±0.0010	0.0018±0.0018
MT	Sabinene	0.015±0.012	0.0063±0.0043	0.048±0.0093	0.0018±0.0017	0.0069±0.0077	0.014±0.015	1.28±0.84
MT	Beta-Pinene	0.49±0.52	0.40±0.38	0.35±0.21	0.027±0.025	0.0045±0.006	0.012±0.011	0.056±0.054
MT	Beta-Myrcene	0.12±0.12	0.11±0.11	0.14±0.16	0.027±0.020	0.0031±0.0017	0.0063±0.0066	0.024±0.014
MT	l-Phellandrene	0.008±0.0074	0.0065±0.0047	0.0057±0.0053	n.d.	0.00028±0.00013	0.00027±0.00014	0.0054±0.0035
MT	Delta 3-Carene	0.0055±0.0067	0.0011±0.00035	0.0045±0.0044	0.0041±0.0047	0.00064±0.00059	0.00045±0.00023	0.00031±0.00018
MT	Alpha-Terpinene	0.0014±0.00097	0.0016±0.0014	0.0046±0.0050	0.00027±0.00023	0.00052±0.00033	0.00038±0.00040	0.011±0.0081
MT	m-Cymene	0.00044±0.0004	0.00013±0.000057	0.00047±0.00026	0.000072±0.000048	0.00032±0.00017	0.00032±0.00031	0.00048±0.00053
MT	p-isopropyl toluene (p-Cymene)	0.025±0.014	0.0052±0.0036	0.019±0.010	0.0011±0.00096	0.0046±0.0044	0.0016±0.0012	0.040±0.034
MT	Limonene	0.91±1.18	n.d.	0.31±0.21	0.025±0.021	0.0051±0.0029	0.0056±0.0052	0.041±0.010
MT	Beta-Phellandrene	n.d.	0.25±0.21	n.d.	n.d.	n.d.	n.d.	n.d.
MT	cis-Ocimene	0.013±0.0056	0.015±0.013	0.0038±0.0026	0.043±0.033	0.0011±0.00087	0.00092±0.00059	0.0042±0.0040
MT	trans-beta-Ocimene	0.00092±0.00044	0.00063±0.00047	0.0018±0.0013	0.81±0.65	0.0047±0.0056	0.0028±0.0027	0.0020±0.00068
MT	Gamma-Terpinene	0.010±0.012	0.0051±0.0039	0.013±0.012	0.0011±0.00077	0.00097±0.00065	0.00082±0.00071	0.024±0.017
MT	Terpinolene	0.0045±0.0019	0.0084±0.0068	0.0086±0.0079	0.0012±0.00058	n.d.	0.00094±0.00081	0.0055±0.0036
MT	(E)-4,8-Dimethyl-1,3,7-nonatriene	n.d.	0.00060±0.00020	0.00056±0.00034	n.d.	0.027±0.032	0.015±0.018	n.d.
MT	Alloocimene	0.0062±0.0018	0.0051±0.0044	0.00049±0.00017	0.10±0.074	0.00022±0.000062	0.00015±0.000071	0.0077±0.0063
MT	2,6-Dimethyl-1,3,5,7-octatetraene, E	n.d.	n.d.	0.00018±0.000069	n.d.	0.00018±0.000058	0.00017±0.00013	n.d.
Total Monoterpenes		**1.66±1.67**	**1.16±0.77**	**2.30±1.28**	**0.88±0.69**	**0.070±0.031**	**0.063±0.069**	**1.30±0.98**

Table 4.1 Continued

SQ	Copaene	0.0033±0.0028	0.014±0.011	0.0026±0.0011	0.00048±0.00028	0.015±0.015	0.0059±0.0068	0.0048±0.0023
SQ	Beta-cubebene	0.00020±0.000081	0.00036±0.00019	0.00032±0.00022	0.00027±0.00024	0.0041±0.0031	0.0013±0.0012	0.0021±0.00063
SQ	Isolongifolene	0.0057±0.0049	0.0057±0.0062	0.027±0.032	0.0047±0.0068	0.0047±0.0055	0.00039±0.00025	0.0056±0.0049
SQ	Alpha-cedrene	0.0016±0.0012	0.0015±0.0019	0.016±0.0093	0.00013±0.000091	0.00044±0.000097	0.00047±0.00021	n.d.
SQ	trans-Caryophyllene	n.d.	0.0021±0.0028	0.0022±0.00065	0.0017±0.0016	0.032±0.048	0.0096±0.011	0.058±0.00028
SQ	Alpha-humulene	0.00020±0.00023	0.0012±0.00028	0.00016±0.000053	0.00017±0.00012	0.015±0.0018	0.0035±0.0048	0.0038±0.00018
SQ	Beta-farnesene	n.d.	n.d.	0.00039±0.00014	n.d.	0.0018±0.00013	0.0010±0.00054	n.d.
SQ	Germacrene-D	n.d.	n.d.	n.d.	0.00023±0.00015	0.0065±0.0064	0.0016±0.0016	0.0044±0.0021
SQ	Alpha-Bergamotene	0.00060±0.00051	0.00085±0.00078	0.00079±0.00064	n.d.	0.00030±0.000098	n.d.	n.d.
SQ	E,E-Alpha-Farnesene	0.00034±0.00033	0.020±0.016	0.00024±0.000040	n.d.	n.d.	0.00048±0.00017	n.d.
SQ	Beta-selinene	0.00030±0.00025	0.013±0.016	0.00052±0.00020	0.00023±0.00021	n.d.	n.d.	n.d.
SQ	Alpha-muurolene	n.d.	0.00088±0.00087	0.000079±0.0000039	0.00057±0.00043	0.0028±0.0025	0.0013±0.00086	0.020±0.0024
SQ	Gamma-cadinene	0.00012±0.000048	0.0017±0.0026	0.00068±0.00014	0.00042±0.00040	0.0040±0.0040	0.0018±0.0013	0.017±0.015
SQ	Alpha-cadinene	0.0033±0.0028	0.014±0.011	0.0026±0.0011	n.d.	0.00061±0.00030	0.00038±0.00021	n.d.
SQ	Cis-Alpha-Bisabolene	0.00020±0.000081	0.00036±0.00019	0.00032±0.00022	n.d.	0.00054±0.000033	0.0003±0.00024	n.d.
Total Sesquiterpenes		**0.0086±0.0072**	**0.074±0.056**	**0.036±0.042**	**0.0060±0.0064**	**0.067±0.067**	**0.022±0.025**	**0.061±0.038**
OX	2-Butanone	n.d.	n.d.	n.d.	0.000084±0.000079	n.d.	n.d.	n.d.
OX	Furan. 2-methyl-	0.00045±0.00032	0.00055±0.00021	0.0027±0.0014	0.00062±0.0003	0.0055±0.0035	0.0030±0.00081	0.00047±0.00032
OX	2-Methyl-3-buten-2-ol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
OX	Crotonaldehyde	0.0057±0.0028	0.0055±0.0020	0.015±0.0048	0.0037±0.0025	0.023±0.012	0.0099±0.0037	0.0042±0.0019
OX	Butyl aldoxime. 3-methyl-. syn-	n.d.	n.d.	n.d.	n.d.	0.001±0.00043	n.d.	n.d.
OX	Isocineole	n.d.	0.00083±0.00051	0.00049±0.000084	n.d.	n.d.	n.d.	0.00029±0.00011
OX	p-Methylanisole	0.00075±0.00044	n.d.	0.00047±0.00027	n.d.	0.00023±0.00011	n.d.	n.d.
OX	Eucalyptol	0.17±0.13	0.028±0.027	0.29±0.11	0.00083±0.0006	0.014±0.016	0.038±0.025	0.020±0.011

Table 4.1 Continued

OX	1-Octanol	0.012±0.0094	0.0029±0.0012	0.0077±0.0029	0.0087±0.0072	0.0021±0.001	0.0025±0.0013	0.012±0.010
OX	Dihydromyrcenol	0.0094±0.0064	0.00052±0.00028	0.0014±0.0011	0.011±0.015	0.00086±0.00011	0.00041±0.00024	0.0057±0.0053
OX	Gamma-Terpineol	0.0092±0.0078	0.014±0.011	0.0086±0.0091	0.010±0.0031	0.00099±0.0004	n.d.	0.035±0.011
OX	L-Fenchone	0.0011±0.0014	0.00038±0.00018	0.0014±0.00040	0.00021±0.00022	n.d.	0.00023±0.00017	0.00072±0.00018
OX	Rosefuran	n.d.	n.d.	n.d.	0.0011±0.000083	0.00063±0.0003	n.d.	n.d.
OX	Tetrahydrolinalool	n.d.	n.d.	0.00046±0.00021	n.d.	n.d.	n.d.	n.d.
OX	Linalool L	n.d.	0.054±0.049	0.031±0.024	0.010±0.0084	0.065±0.06	0.019±0.012	0.018±0.014
OX	D-Fenchyl alcohol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
OX	2-Methyl-6-methylene-1,7-octadien-3-one	0.0075±0.0074	0.00050±0.00027	0.0015±0.00050	n.d.	n.d.	n.d.	n.d.
OX	2-tert-Butylcyclohexanone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
OX	trans-Dihydro-b-terpineol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
OX	Camphor	0.0050±0.0039	0.00081±0.0010	0.097±0.11	0.00043±0.00028	0.0010±0.00085	0.0012±0.00066	0.0013±0.0013
OX	Isoborneol	0.0059±0.0048	0.00021±0.000036	0.014±0.0055	n.d.	0.0023±0.0034	0.0020±0.0012	n.d.
OX	d-Pinocarvone	0.015±0.011	0.00058±0.00049	0.0052±0.0026	0.0023±0.0023	0.0010±0.00042	n.d.	0.0012±0.0017
OX	2-(1,1-dimethylethyl)-cyclohexanol	n.d.	n.d.	n.d.	0.0025±0.0021	n.d.	n.d.	n.d.
OX	4-Terpineol	0.062±0.070	0.020±0.020	0.017±0.021	n.d.	0.0012±0.00081	0.00077±0.00052	0.063±0.036
OX	Alpha-Terpineol	0.28±0.30	0.015±0.016	0.038±0.032	0.0069±0.005	0.0051±0.0023	0.0042±0.0053	0.024±0.015
Total Oxygenated Compounds		**0.55±0.45**	**0.13±0.11**	**0.50±0.20**	**0.033±0.021**	**0.090±0.058**	**0.060±0.040**	**0.16±0.053**
OX-SQ	Methyl Eugenol	0.00029±0.00030	0.00022±0.000037	0.00015±0.000049	0.00042±0.00012	0.00038±0.00026	0.00017±0.00012	n.d.
OX-SQ	(-)-Spathulenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
OX-SQ	Guaiol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Total Oxygenated Sesquiterpenes		**0.00024±0.00030**	**0.00011±0.00012**	**0.00012±0.000074**	**0.00014±0.00022**	**0.00032±0.00028**	**0.000086±0.00012**	**n.d.**

n.d.: Not detected.

Table 4.2 Categorized emission factors

BVOC Group	Troy Fir	Cilician Fir	Uludag Fir	Boz Pirnal Oak	Ispir Oak	Vulcanic Oak	Oriental Sweetgum
Basis on dried leaf weight (µg g^{-1} h^{-1})							
Isoprene	1.34±1.11	14.1±10.5	1.50±1.39	0.028±0.026	19.2±19.0	9.79±7.57	15.0±15.2
Monoterpenes	1.66±1.67	1.16±0.77	2.30±1.28	0.88±0.69	0.070±0.031	0.063±0.069	1.30±0.98
Sesquiterpenes	0.0086±0.0072	0.074±0.056	0.036±0.042	0.0060±0.0064	0.067±0.067	0.022±0.025	0.061±0.038
Oxygenated sesq.	0.00024±0.00030	0.00011±0.00012	0.00012±0.000074	0.00014±0.00022	0.00032±0.00028	0.000086±0.00012	n.d.
Oxygenated comp.	0.55±0.45	0.13±0.11	0.50±0.20	0.033±0.021	0.090±0.058	0.060±0.040	0.16±0.053
Total	3.56±3.24	15.5±11.5	4.34±2.92	0.94±0.74	19.4±19.1	9.93±7.71	16.5±16.3
Basis on net leaf area (µg m^{-2} h^{-1})							
Isoprene	395±279	5472±3559	567±552	7.06±6.22	2745±2623	1193±927	1240±1248
Monoterpenes	584±665	466±290	906±634	232±182	10.9±5.36	7.83±8.71	103±81.3
Sesquiterpenes	2.95±2.20	29.9±21.7	13.7±16.8	1.55±1.63	9.12±9.05	2.66±3.04	5.13±3.47
Oxygenated sesq.	0.073±0.088	0.050±0.050	0.043±0.027	0.035±0.056	0.048±0.041	0.010±0.015	n.d.
Oxygenated comp.	184±144	53±44.4	181±84.3	8.61±5.60	15.6±7.00	7.28±4.99	13.5±4.50
Total	1167±1091	6021±3915	1669±1286	249±195	2781±2645	1210±944	1361±1337

n.d.: Not detected.

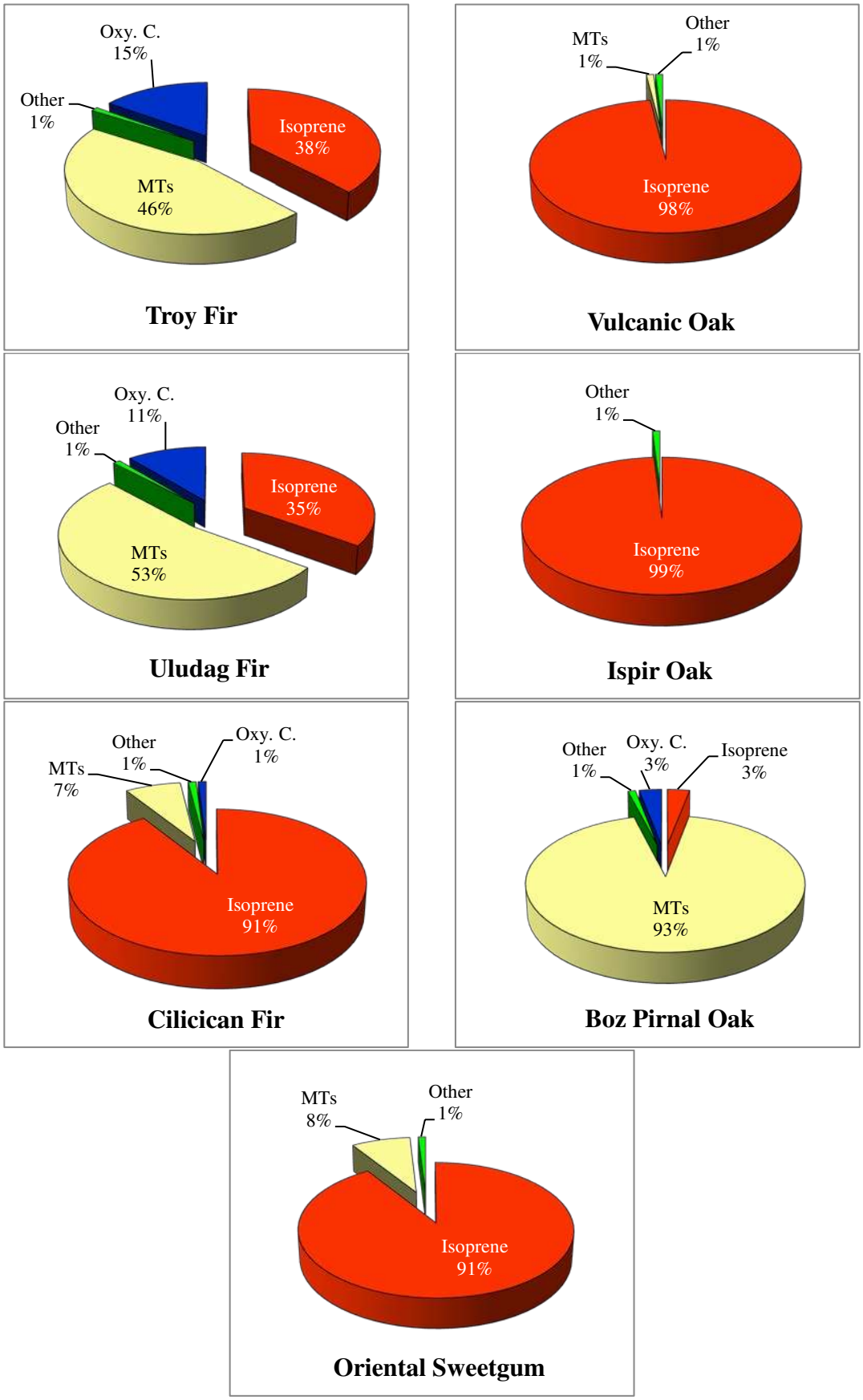

Figure 4.1 Emission compositions of the investigated species.

The ratio of monoterpenes to sesquiterpenes was different among the species. The ratio ranged from 1 to 193 for Ispir Oak and Troy Fir, respectively. The composition pattern could be classified into three types; monoterpene-rich group (Troy Fir, Boz Pirnal Oak), sesquiterpene-rich group (Vulcanic Oak, Ispir Oak), and the intermediate group (other four species).

4.2 Characterization of BVOC Emissions

Alpha-pinene, beta-pinene, beta-myrcene and limonene are the most characteristic compounds specifying the general monoterpene emission profiles (see Table 4.1 and Figure 4.2). Limonene was emitted by all trees except Cilician Fir, while beta-phellandrene was emitted only by Cilician Fir. Monoterpene emissions of Boz Pirnal Oak and Oriental Sweetgum mainly consist of trans-beta-ocimene (77%) and sabinene (82%), respectively. As previously mentioned in Section 3.1, Oriental Sweetgum is a featured tree with its unique essential oils and secretions used for medicinal purposes, therefore, sabinene might be a marker compound of these extracts. Even they showed lower contributions to total emissions, trans-caryophyllene, isolongifolene, alpha-humulene and copaene are the prominent sesquiterpenes (see Figure 4.3). As shown in Figure 4.4, predominant oxygenated compounds were eucalyptol, linalool-L and alpha-terpineol; however no linalool-L emission was detected from Troy Fir.

Fir species are mostly known as monoterpene emitters with the remarkable compounds; alpha-pinene, beta-pinene, limonene and camphene, while relatively low isoprene emissions were reported in previous studies (Moukhtar, Couret, Rouil, & Simon, 2006; Dominguez-Taylor et al., 2007). Two of the fir species (Uludag Fir and Troy Fir) investigated in this study clearly showed a similar tendency. Monoterpenes had the highest portion with nearly 50% of all BVOC emissions for these species as indicated in Figure 4.1. Pokorska et al. (2012a) reported that 0.742, 0.917, 0.429 and 0.512 $\mu g\ g^{-1}\ h^{-1}$ of alpha-pinene, camphene, beta-pinene and limonene emitted from Silver Fir (*Abies alba*), respectively in Belgium. In the present study, 0.18 and 1.44 $\mu g\ g^{-1}\ h^{-1}$ of alpha-pinene, 0.91 and 0.31 $\mu g\ g^{-1}\ h^{-1}$ of limonene, 0.49 and

0.35 µg g^{-1} h^{-1} of beta-pinene were determined for Troy Fir and Uludag Fir, respectively. In contrast, Cilician Fir was determined as an isoprene emitter. Although it has a high isoprene ratio of 91.2%, it still emits considerable amounts of monoterpenes as much as the other fir species. Similarly, Harrison et al. (2001) reported average annual isoprene and monoterpene emission factors of 18.4±3.8 µg g^{-1} h^{-1} and 2.7±1.1 µg g^{-1} h^{-1} respectively for Bulgarian Fir (*Abies borisii-regis*) which is endemic to Balkans. Table 4.3 shows these comparisons in detail.

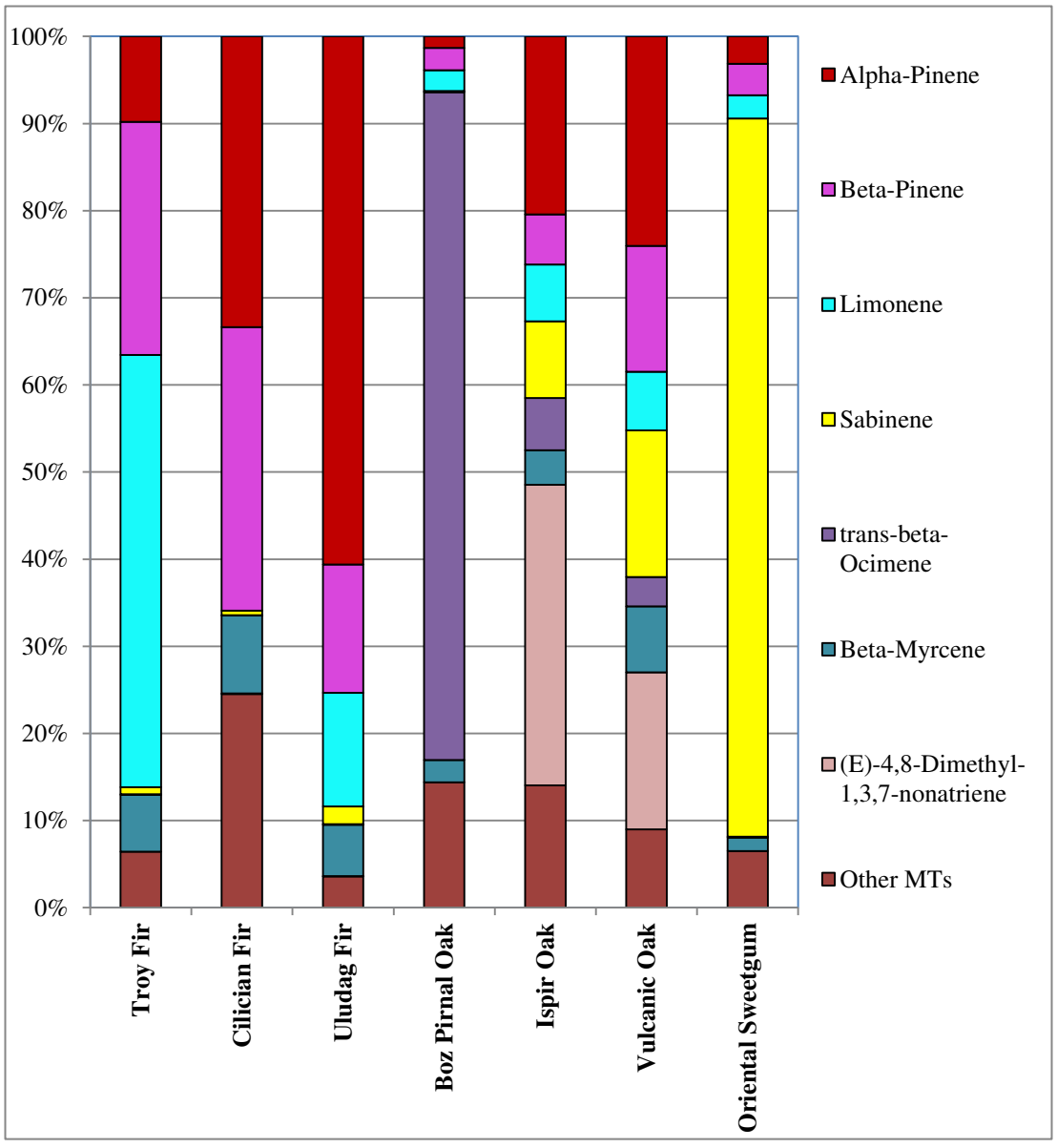

Figure 4.2 Percentages of the most prominent monoterpenes.

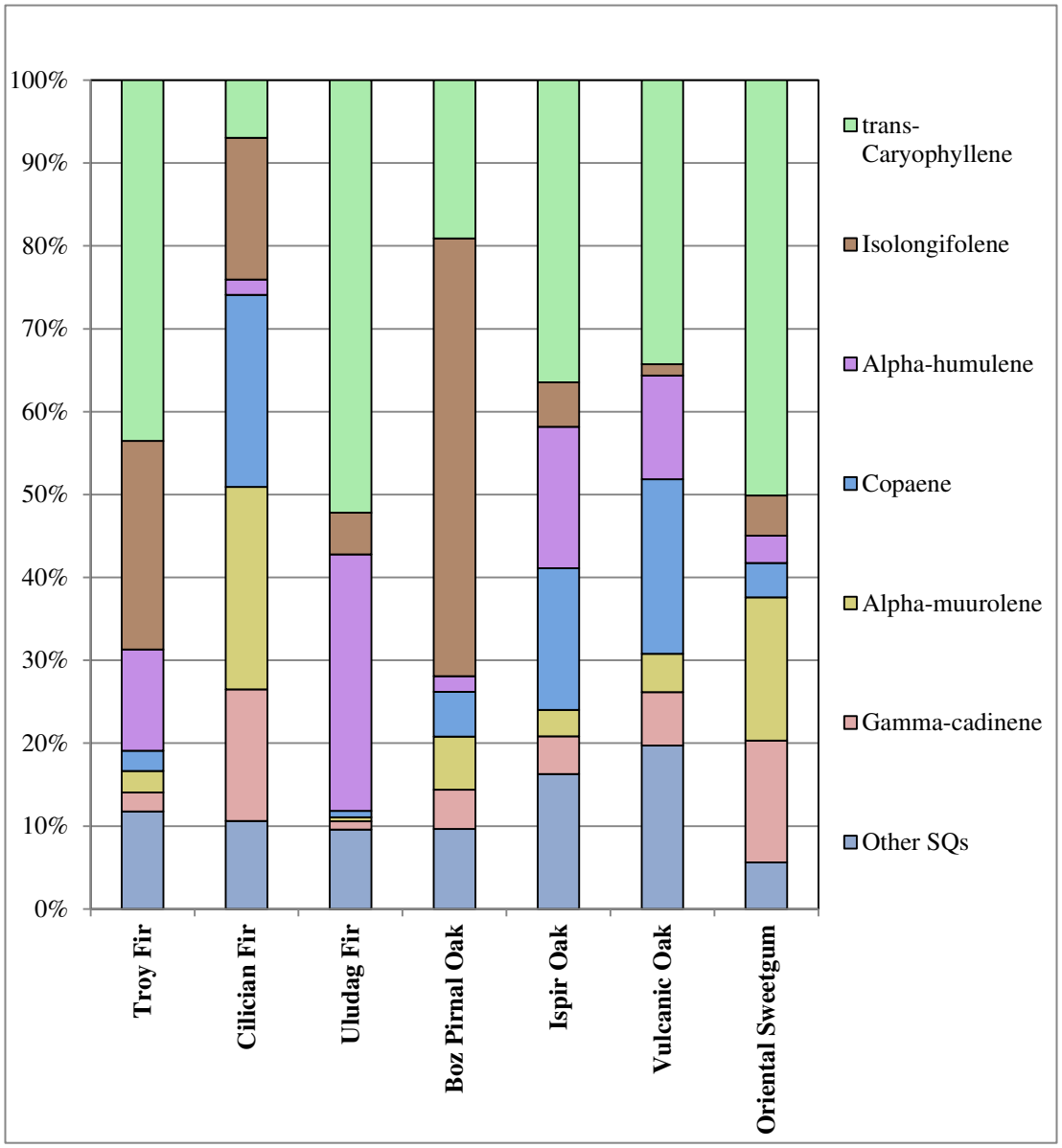

Figure 4.3 Percentages of the most prominent sesquiterpenes.

Oak species are strong isoprene emitters as broadleaved trees. However, a considerable variation was observed within the reported values in literature (see Table 4.3). In previous studies, researchers have commonly focused on isoprene emissions for oak species and therefore, rarely determined the emission factors for monoterpenes or any other BVOCs. Two of three studied oak species (Vulcanic Oak and Ispir Oak) were exhibited the typical emitting characteristics of the genus, however, Boz Pirnal Oak was different with substantially lower isoprene emission (0.028 ± 0.026 µg g^{-1} h^{-1}). Although the monoterpene emission factor was also relatively low (0.88 ± 0.69 µg g^{-1} h^{-1}), its contribution (about 93%) to total BVOCs

makes the tree a monoterpene emitter. Another oak species, Holly Oak (*Quercus ilex*) is one of the most widely investigated in previous studies (Street, Owen, Duckham, Boissard & Hewitt, 1997; Loreto et al., 1998; Grote et al., 2006) due to its prominently high monoterpene emitting potentials.

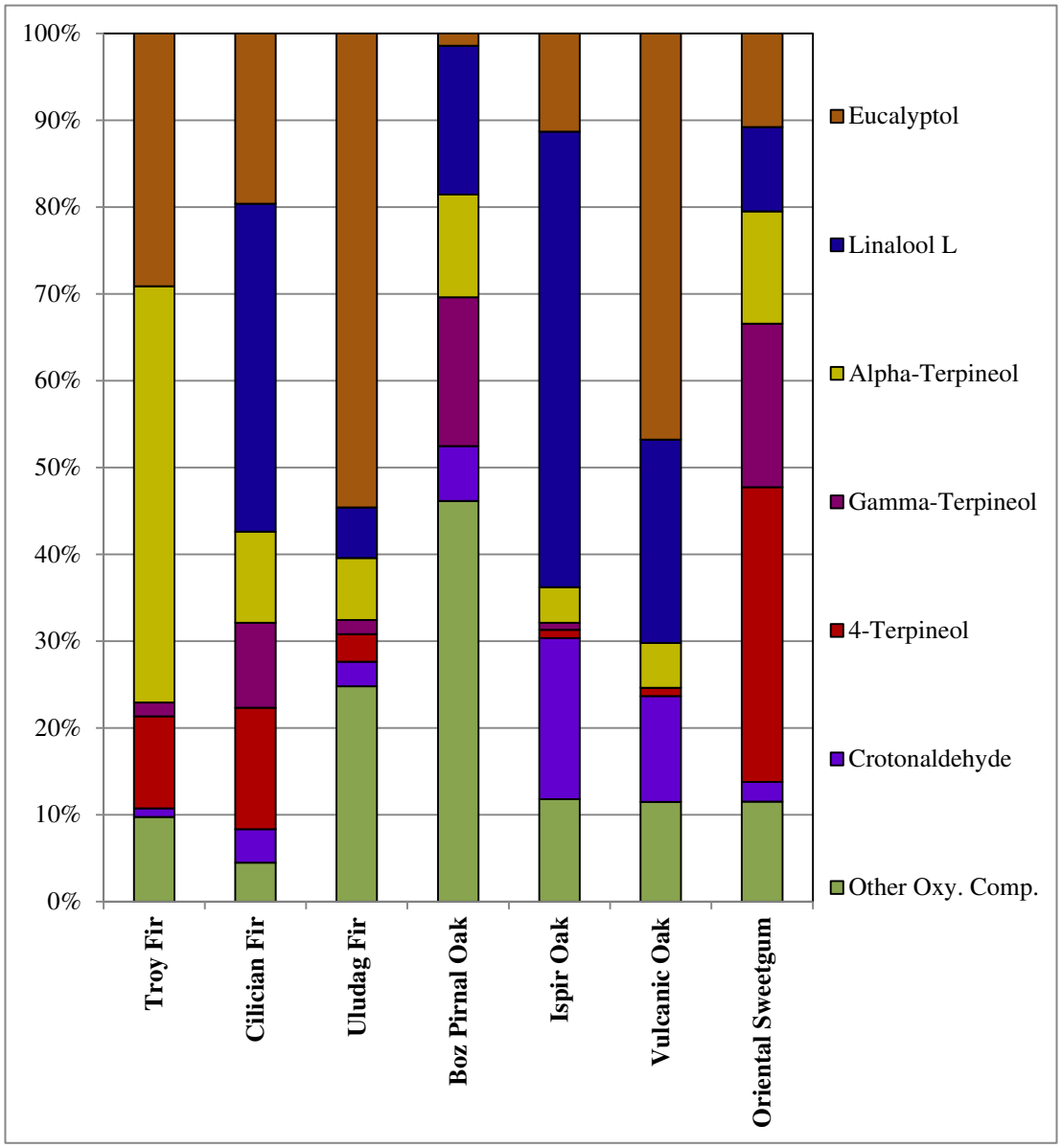

Figure 4.4 Percentages of the most prominent oxygenated compounds.

Differences in BVOC emission characteristics of the congeners in this study might be resulted from anatomical variations and/or biotope conditions. Cilician Fir had geographically different habitat conditions. It grows on lime-soils at southern latitudes while the others prefer humid and acidic soils of northern

latitudes. This might affect the BVOC emission compositions. Relatively high isoprene emissions for fir species were also reported by some other researchers (Harrison et al., 2001; Pokorska et al., 2012a). Rasmussen (1978) conducted a detailed survey on tree species to determine isoprene emissions. Silver Fir and Grecian Fir (*Abies cephalonica*) were shown to emit isoprene, but, any emission rate was not reported. Presently, there is no specified parameter that could be related to these unusual emitting behaviors. However, habitat conditions, growing stages, metabolic and enzymatic processes, unidentified stress factors or genetic constitutions might be effective (Street et al., 1997; Fall, 1999; Kim et al., 2005; Singh, Varshney, & Singh, 2007; Joo et al., 2010). On the other hand, as an evergreen tree, Boz Pirnal Oak is anatomically dissimilar to the other two studied deciduous oaks. It is a quite small shrub-like tree, reaching a maximum height of 5-6 meters and prefers low altitudes and high temperature zones. Therefore, emissions of Boz Pirnal Oak did not show similarities with Vulcanic Oak and Ispir Oak. Another oak species, Kermes Oak (*Quercus coccifera*) has similar characteristics with Boz Pirnal Oak, was also reported as a low BVOC emitter (Dasdemir et al., 2012). Likewise, Vulcanic Oak and Ispir Oak were also physically comparable with some massive oaks previously investigated in the literature such as Pedunculate Oak (*Quercus robur*) and Sessile Oak (*Quercus petraea*) with their typically high-isoprene and low-monoterpene emission patterns (see Table 4.3). Furthermore, monoterpene, sesquiterpene and oxygenated compound compositions of these species were mainly consist of the same predominant compounds as illustrated in Figures 3, 4 and 5.

Based on their studies on several oak species Loreto et al. (1998) and Loreto (2002) have concluded that (i) oaks grown in the western hemisphere emit mainly isoprene; (ii) monoterpene emission is specific to evergreen oaks of the Mediterranean environment; (iii) another group of Mediterranean oaks does not emit isoprenoids in substantial amounts; and (iv) the differences in emission profiles generally matches the taxonomical classification of oaks based on anatomical or molecular markers. The emission profiles for different oak species observed in the present study were in close agreement with these findings.

Table 4.3 Comparison of the emission factors previously reported in the literature (at 1000 µmol m^{-2} s^{-1} and 30°C)

Common Name	Genus/Species	Distribution Region	Emission Factor (µg g^{-1} h^{-1})			Number of Samples	Reference
			Isoprene	Monoterpenes	Sesquiterpenes		
Silver Fir	*Abies alba*	Europe	<0.1	0.63	n.r.	62	1
			1	1	0.1	n.r.	2
			4.6 – 27	0.26 – 2.85[a]		18	3
Sacred Fir	*Abies religiosa*	Mexico	n.d.	6.066	n.r.	12	4
Bulgarian Fir	*Abies borisii-regis*	Balkans	18.4±3.8	2.7±1.1	n.r.	n.r.	5
Balsam Fir	*Abies balsamea*	intercontinental	n.r.	3.40±2.60	<0.01	5	6
Grand Fir	*Abies grandis*	N.W. of the USA	n.r.	0.36±0.27	0.01±0.01	15	6
Greek Fir	*Abies cephalonica*	Greece	n.r.	0.63	0.1	n.r.	2
Troy Fir	*Abies equi-trojani*	Turkey	1.34±1.11	1.66±1.67	0.0086±0.0072	6	This study.
Cilician Fir	*Abies cilic. subsp. isaur.*	Turkey	14.1±10.5	1.16±0.77	0.074±0.056	6	This study.
Uludag Fir	*Abies nord. subsp. born.*	Turkey	1.50±1.39	2.30±1.28	0.036±0.042	6	This study.
Holly Oak	*Quercus ilex*	Mediteranean Region	0.1	43	0.1	n.r.	2
			0.007±0.011	12.0±12.7	n.r.	n.r.	7
			n.r.	21.7±2.00	n.r.	n.r.	8
			n.r.	21.1±19.8	n.r.	115	9
			n.r	17.5±10.2	n.r.	7 to 15	10
Sessile Oak	*Quercus petraea*	Europe and Anatolia	6.14±4.95	0.0094±0.0036	0.0050±0.0030	6	11
			43	0.1	0.1	n.r.	2
			<0.17 – 7.05	n.r.	n.r.	n.r.	12
			0.61	0.12	n.r.	2	13

Table 4.3 Continued

Pendunculate Oak	*Quercus robur*	Europe, Anatolia,	58.28	0.68	n.r	n.r.	14
		Caucasus and	70	1	0.1	n.r.	2
		N. Africa	61	0.23	n.r	77[b]	3
Hungarian Oak	*Quercus frainetto*	S.E. of Europe, Balkans	85	n.r.	0.1	n.r.	2
		and Turkey	133.95	n.r.	n.r.	n.r.	12
Canyon Live Oak	*Quercus chrysolepis*	California, Mexico	48	n.r.	n.r.	10	15
Valley Oak	*Quercus lobata*	California	86	n.r.	n.r.	14	15
Kermes Oak	*Quercus coccifera*	Mediteranean Region and N. Africa	n.d.	0.0009	n.r.	1	16
n.r.	*Quercus rotundifolia*	South Europe, Algeria, N. Africa	0.2	14.6	0.1	n.r.	2
North. Red Oak	*Quercus rubra*	North America	35	0.1	0.1	n.r.	2
Downy Oak	*Quercus pubescens*	South Europe and Southwest Asia	70	0.3	0.1	n.r.	2
Vulcanic Oak	*Quercus vulcanica*	Turkey	9.79±7.57	0.063±0.070	0.022±0.025	6	This study.
Ispir Oak	*Quercus macr. subsp. syspir.*	Turkey	19.2±19.0	0.070±0.031	0.067±0.068	6	This study.
Boz Pirnal Oak	*Quercus aucheri*	Turkey	0.028±0.026	0.88±0.69	0.0060±0.0064	6	This study.
American Sweetgum	*Liquidambar styraciflua*	North and Central	29.0±16.5	n.r.	n.r.	15-17	17
		America	68	n.r.	n.r.	11	15
Oriental Sweetgum	*Liquidambar orientalis*	Turkey	15.0±15.2	1.30±0.98	0.061±0.038	6	This study.

n.d.: not detected, n.r.: not reported, a: The reported value refers to sum of monoterpenes and sesquiterpenes, b: Sum of the collected number of samples for studied two tree species (*Q. robur* and *F. excelsior*). References: [1]:Moukhtar et al. (2006); [2]: Steinbrecher et al. (2009); [3]:Pokorska et al., (2012a); [4]:Dominguez-Taylor et al. (2007); [5]: Harrison et al. (2001); [6]: Ortega et al. (2008);[7]: Owen et al. (1997); [8]: Bertin et al. (1997) [9]: Sabillon & Cremades (2001); [10]: Kesselmeier et al. (1998); [11]: Elbir et al. (2013); [12]: Steinbrecher et al. (1997); [13]: Konig et al. (1995); [14]: Perez-Rial, Penuelas, Lopez-Mahia, & Llusia (2009); [15]: Geron, Harley, Guenther (2001) [16]: Dasdemir et al. (2012); [17]: Harley, Guenther, Zimmerman (1996)

CHAPTER FIVE
CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions and Recommendations

BVOC emissions of seven endemic tree species of Turkey were investigated in this study. On-site measurements were conducted in natural habitats of each species following the dynamic branch enclosure method. Samplings were achieved for three representative trees for each species and collected samples were analyzed with a GC/MS system equipped with a thermal desorber.

As largely reported in literature, isoprene and monoterpenes were predominant compounds for all species. Fir and Oak species were prone to emit monoterpenes and isoprene respectively. The highest isoprene and monoterpene emissions were emitted by Ispir Oak and Uludag Fir with the emission rates of 19.2±19.0 and 2.30±1.28 $\mu g\ g^{-1}\ h^{-1}$ respectively. Oxygenated compounds were ranked as the third most prominent group and sesquiterpenes had slightly lower portions with a maximal value of 0.074±0.056 $\mu g\ g^{-1}\ h^{-1}$ for Cilician Fir which covers only ~0.5% of sum of its emissions. Although two of the three fir species showed similar emitting behaviors, Cilician Fir had completely different emission composition. Additionally, Boz Pirnal Oak had also exceptional pattern. Physiologically both the two trees had varied features make them incompatible with their congeners in this study. However, there were many plant species reported with unexpected emission behaviors in previous studies and also the values determined even for same species mostly include differences.

As previously mentioned, BVOCs are synthesized and emitted to the atmosphere under the effect of several parameters such as biotic and abiotic stress sources, environmental conditions, growing stages, biological cycles and gene expressions. Although some of these parameters are manageable during the samplings, it is usually impossible to interfere biological processes that are controlled by genes. Some unusual emission behaviors observed in this study

were also probably caused by undefined/uncontrollable stress factors and/or genetic alterations those related to metabolic processes. For future studies, considering more effective parameters, properly controlled stress factors, long-term measurements, multi-disciplinary (botany, biology, plant physiology etc.) approaches from different aspects can minimize the uncertainties and improve the stability of the results.

BVOC emissions of endemic tree species in Turkey were characterized for the first time in the present study. These specific emission factors could be utilized in the future BVOC inventories and air quality modeling studies. However, these results based on three sample trees for each species those grown in studied regions and environmental conditions and biological cycles of the sampling periods. Thereby, it should be noted that using of these emission factors without considering the uncertainties discussed above may cause over/underestimations in future studies.

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APPENDICES

Appendix A

Leaf Area Based Emission Factors

(in µg m^{-2} h^{-1})

Table A.1 BVOC emission factors (average±standard deviation) for the trees (µg m^{-2} h^{-1}) at standard conditions (at 1000 µmol m^{-2} s^{-1} and 30°C)

Group	Compound	Troy Fir	Cilician Fir	Uludag Fir	Boz Pirnal Oak	Ispir Oak	Vulcanic Oak	Oriental Sweetgum
Isoprene	**Isoprene**	**395±279**	**5472±3559**	**567±552**	**7.06±6.22**	**2745±2623**	**1193±927**	**1240±1248**
MT	Tricyclene	1.52±1.27	0.19±0.070	0.54±0.36	0.14±0.22	0.073±0.066	0.032±0.037	0.012±0.0050
MT	Alpha-Pinene	56±12.8	168±131	521±363	3.67±0.34	2.51±3.17	2.49±2.28	3.88±3.66
MT	Alpha-Fenchene	0.85±0.90	0.14±0.042	0.18±0.081	0.050±0.022	n.d.	n.d.	0.014±0.0039
MT	Camphene	12.9±8.86	1.01±0.63	8.04±4.27	0.17±0.14	0.27±0.19	0.14±0.13	0.15±0.15
MT	Sabinene	5.23±4.17	2.51±1.55	17.1±4.52	0.47±0.44	1.11±1.31	1.73±1.84	103±66.9
MT	Beta-Pinene	186±214	158±142	178±151	6.86±6.56	1.32±1.70	1.46±1.46	2.98±2.47
MT	Beta-Myrcene	42.3±47.4	42.7±42.0	50.4±58.4	6.84±4.95	0.47±0.26	0.78±0.81	1.89±1.07
MT	l-Phellandrene	2.65±2.74	2.58±1.69	1.99±1.96	n.d.	0.042±0.020	0.033±0.018	0.43±0.29
MT	Delta 3-Carene	1.66±1.65	0.47±0.13	1.56±1.48	1.05±1.21	0.098±0.090	0.054±0.028	0.025±0.015
MT	Alpha-Terpinene	0.45±0.31	0.66±0.54	1.72±2.00	0.074±0.066	0.081±0.056	0.047±0.049	0.91±0.67
MT	m-Cymene	0.14±0.13	0.054±0.026	0.21±0.13	0.019±0.013	0.049±0.026	0.040±0.040	0.04±0.043
MT	p-isopropyl toluene (p-Cymene)	8.66±5.55	2.03±1.28	6.57±3.31	0.30±0.27	0.46±0.39	0.19±0.16	3.32±2.8
MT	Limonene	321±465	n.d.	113±79.5	6.61±5.93	0.78±0.44	0.69±0.64	3.30±0.77
MT	Beta-Phellandrene	n.d.	100±83.7	n.d.	n.d.	n.d.	n.d.	n.d.
MT	cis-Ocimene	4.00±1.25	6.31±5.27	1.8±0.52	11.0±7.88	0.17±0.12	0.11±0.072	0.33±0.32
MT	trans-beta-Ocimene	0.28±0.13	0.25±0.18	0.64±0.43	214±167	0.73±0.91	0.34±0.34	0.16±0.053
MT	Gamma-Terpinene	1.97±2.18	2.08±1.50	4.72±4.67	0.29±0.23	0.15±0.10	0.10±0.088	1.97±1.36
MT	Terpinolene	1.48±0.81	3.34±2.48	3.20±3.13	0.33±0.17	n.d.	0.11±0.10	0.45±0.29
MT	(E)-4,8-Dimethyl-1,3,7-nonatriene	n.d.	0.26±0.080	0.19±0.11	n.d.	3.75±4.49	1.90±2.16	n.d.
MT	Alloocimene	2.03±0.65	2.08±1.79	0.18±0.063	27.0±21.0	0.033±0.0061	0.017±0.0069	0.64±0.52
MT	2,6-Dimethyl-1,3,5,7-octatetraene, E	n.d.	n.d.	0.055±0.014	n.d.	0.028±0.011	0.021±0.016	n.d.
Total Monoterpenes		**584±665**	**466±290**	**906±634**	**232±182**	**10.9±5.36**	**7.83±8.71**	**103±81.3**

Table A.1 Continued

SQ	Copaene	0.18±0.20	7.48±5.76	0.15±0.059	0.13±0.074	1.51±1.32	0.73±0.83	0.39±0.19
SQ	Beta-cubebene	0.14±0.12	0.62±0.53	0.12±0.036	0.072±0.068	0.63±0.49	0.16±0.14	0.17±0.048
SQ	Isolongifolene	1.16±0.96	5.49±4.32	0.92±0.40	1.21±1.71	0.69±0.80	0.045±0.029	0.46±0.40
SQ	Alpha-cedrene	0.07±0.0093	0.15±0.068	0.12±0.067	0.034±0.025	0.068±0.0054	0.057±0.029	n.d.
SQ	trans-Caryophyllene	1.74±1.35	2.37±2.39	10.2±12.6	0.44±0.43	4.85±6.91	1.13±1.28	4.98±0.44
SQ	Alpha-humulene	0.47±0.32	0.60±0.73	6.18±3.96	0.042±0.027	1.70±1.19	0.42±0.57	0.31±0.017
SQ	Beta-farnesene	n.d.	0.81±1.08	0.83±0.20	n.d.	0.25±0.026	0.12±0.062	n.d.
SQ	Germacrene-D	0.089±0.10	0.49±0.083	0.058±0.016	0.059±0.037	1.07±1.14	0.19±0.19	0.36±0.15
SQ	Alpha-Bergamotene	n.d.	n.d.	0.14±0.060	n.d.	0.045±0.0069	n.d.	n.d.
SQ	E,E-Alpha-Farnesene	n.d.	n.d.	n.d.	n.d.	n.d.	0.062±0.024	n.d.
SQ	Beta-selinene	0.18±0.14	0.57±0.56	0.27±0.21	0.060±0.051	n.d.	n.d.	n.d.
SQ	Alpha-muurolene	0.22±0.24	8.1±5.86	0.081±0.013	0.15±0.12	0.43±0.41	0.15±0.099	1.66±0.24
SQ	Gamma-cadinene	0.11±0.10	5.29±6.34	0.19±0.081	0.11±0.10	0.58±0.55	0.21±0.15	1.39±1.28
SQ	Alpha-cadinene	n.d.	0.33±0.31	0.027±0.00061	n.d.	0.092±0.045	0.044±0.025	n.d.
SQ	Cis-Alpha-Bisabolene	0.045±0.027	0.68±1.01	0.25±0.026	n.d.	0.075±0.0071	0.034±0.025	n.d.
Total Sesquiterpenes		**2.95±2.20**	**29.9±21.7**	**13.7±16.8**	**1.55±1.63**	**9.12±9.05**	**2.66±3.04**	**5.13±3.47**
OX	2-Butanone	n.d.	n.d.	n.d.	0.021±0.019	n.d.	n.d.	0.038±0.026
OX	Furan. 2-methyl-	0.13±0.092	0.22±0.061	0.96±0.50	0.16±0.072	0.80±0.50	0.36±0.11	n.d.
OX	2-Methyl-3-buten-2-ol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.35±0.15
OX	Crotonaldehyde	1.86±0.98	2.23±0.64	5.41±1.51	0.96±0.62	3.33±1.58	1.18±0.47	n.d.
OX	Butyl aldoxime. 3-methyl-. syn-	n.d.	n.d.	n.d.	n.d.	0.15±0.062	n.d.	0.024±0.0091
OX	Isocineole	n.d.	0.33±0.18	0.18±0.053	n.d.	n.d.	n.d.	n.d.
OX	p-Methylanisole	0.26±0.17	n.d.	0.13±0.064	n.d.	0.033±0.015	n.d.	1.63±0.88
OX	Eucalyptol	53.5±38.2	10.8±10.8	103±43.3	0.22±0.17	4.68±5.63	4.72±3.25	0.99±0.86

Table A.1 Continued

OX	1-Octanol	4.48±4.34	1.19±0.41	2.71±1.02	2.22±1.70	0.33±0.18	0.31±0.17	0,47±0,44
OX	Dihydromyrcenol	3.03±1.71	0.21±0.093	0.48±0.36	2.81±3.68	0.13±0.026	0.049±0.029	2,91±1,07
OX	Gamma-Terpineol	3.08±2.71	5.39±4.08	3.19±3.56	2.82±0.93	0.15±0.083	n.d.	0,058±0,015
OX	L-Fenchone	0.34±0.43	0.15±0.082	0.50±0.11	0.055±0.056	n.d.	0.029±0.023	n.d.
OX	Rosefuran	n.d.	n.d.	n.d.	0.27±0.050	0.097±0.051	n.d.	n.d.
OX	Tetrahydrolinalool	n.d.	n.d.	0.16±0.068	n.d.	n.d.	n.d.	1,47±1,10
OX	Linalool L	n.d.	21.1±19.1	11.5±8.71	2.72±2.09	9.23±8.04	2.20±1.39	n.d.
OX	D-Fenchyl alcohol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
OX	2-Methyl-6-methylene-1,7-octadien-3-one	2.61±2.91	0.21±0.10	0.52±0.17	n.d.	n.d.	n.d.	n.d.
OX	2-tert-Butylcyclohexanone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
OX	trans-Dihydro-b-terpineol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0,10±0,10
OX	Camphor	1.59±1.04	0.31±0.40	35.5±42.5	0.11±0.072	0.17±0.15	0.15±0.082	n.d.
OX	Isoborneol	1.65±1.37	0.083±0.016	4.97±1.70		0.37±0.57	0.25±0.13	0,095±0,14
OX	d-Pinocarvone	5.08±3.00	0.23±0.19	1.83±0.89	0.60±0.58	0.14±0.066	n.d.	n.d.
OX	2-(1,1-dimethylethyl)-cyclohexanol	n.d.	n.d.	n.d.	0.69±0.55	n.d.	n.d.	5,26±3,10
OX	4-Terpineol	21.0±23.2	8.05±7.88	6.35±8.55	n.d.	0.20±0.16	0.092±0.066	1,92±1,15
OX	Alpha-Terpineol	95.1±102	6.11±6.27	14.0±12.6	1.85±1.36	0.78±0.24	0.54±0.69	0,038±0,026
Total Oxygenated Compounds		**184±144**	**53±44.4**	**181±84.3**	**8.61±5.60**	**15.6±7.00**	**7.28±4.99**	**13.5±4.50**
OX-SQ	Methyl Eugenol	0.088±0.089	0.074±0.041	0.052±0.018	0.11±0.022	0.058±0.037	0.020±0.015	n.d.
OX-SQ	(n.d.)n.d.Spathulenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
OX-SQ	Guaiol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Total Oxygenated Sesquiterpenes		**0.073±0.088**	**0.050±0.050**	**0.043±0.027**	**0.035±0.056**	**0.048±0.041**	**0.010±0.015**	**n.d.**

n.d.: Not detected.

Appendix B

Raw Emission Factors Under Experimental Conditions

Table B.1 Raw BVOC emission factors (average±standard deviation) for the trees (µg g^{-1} h^{-1}) under experimental conditions

Group	Compound	Troy Fir	Cilician Fir	Uludag Fir	Boz Pirnal Oak	Ispir Oak	Vulcanic Oak	Oriental Sweetgum
Isoprene	**Isoprene**	**2.25±2.23**	**13.7±7.95**	**1.81±1.65**	**0.052±0.05**	**18.7±20.3**	**11.9±11.7**	**21.4±20.2**
MT	Tricyclene	0.0085±0.0092	0.0005±0.00026	0.0017±0.0010	0.0014±0.0022	0.00054±0.00047	0.00019±0.00012	0.0006±0.00021
MT	Alpha-Pinene	0.28±0.12	0.45±0.35	1.27±0.71	0.047±0.0061	0.019±0.025	0.02±0.013	0.19±0.21
MT	Alpha-Fenchene	0.0054±0.006	0.00047±0.00027	0.00056±0.00022	0.00057±0.00016	n.d.	n.d.	0.00072±0.000012
MT	Camphene	0.058±0.035	0.0028±0.0020	0.026±0.012	0.0021±0.0018	0.002±0.0016	0.00081±0.00057	0.0061±0.0055
MT	Sabinene	0.022±0.017	0.010±0.0091	0.059±0.0049	0.006±0.0057	0.007±0.0085	0.0078±0.0069	5.22±4.7
MT	Beta-Pinene	0.41±0.31	0.74±0.81	0.39±0.23	0.087±0.085	0.0045±0.0065	0.0075±0.0067	0.21±0.21
MT	Beta-Myrcene	0.20±0.19	0.12±0.12	0.16±0.19	0.12±0.11	0.0029±0.0018	0.0076±0.0097	0.091±0.071
MT	l-Phellandrene	0.012±0.011	0.0070±0.0051	0.0067±0.0065	n.d.	0.00032±0.00017	0.00029±0.00016	0.02±0.018
MT	Delta 3-Carene	0.0076±0.0094	0.0015±0.00084	0.0053±0.0049	0.013±0.016	0.00055±0.00048	0.00068±0.00036	0.0013±0.0009
MT	Alpha-Terpinene	0.0022±0.0012	0.0018±0.0018	0.0052±0.0055	0.00083±0.00066	0.00055±0.00043	0.0005±0.00056	0.043±0.04
MT	m-Cymene	0.00043±0.00029	0.00014±0.000062	0.00055±0.00032	0.00022±0.00017	0.00031±0.00017	0.00019±0.00016	0.00084±0.00082
MT	p-isopropyl toluene (p-Cymene)	0.040±0.025	0.0054±0.0038	0.022±0.012	0.0034±0.0032	0.0049±0.0049	0.0011±0.00056	0.085±0.047
MT	Limonene	2.74±3.61	n.d.	0.36±0.25	0.074±0.061	0.004±0.0021	0.0034±0.0018	0.14±0.051
MT	Beta-Phellandrene	n.d.	0.27±0.24	n.d.	n.d.	n.d.	n.d.	n.d.
MT	cis-Ocimene	0.019±0.0080	0.017±0.014	0.0043±0.0032	0.12±0.089	0.001±0.00085	0.00093±0.00061	0.026±0.03
MT	trans-beta-Ocimene	0.0014±0.00055	0.00069±0.00054	0.002±0.0014	2.28±1.52	0.0047±0.0058	0.0031±0.0037	0.007±0.0033
MT	Gamma-Terpinene	0.014±0.014	0.0056±0.0046	0.014±0.013	0.0032±0.002	0.001±0.00083	0.00055±0.00038	0.093±0.082
MT	Terpinolene	0.0070±0.0025	0.0094±0.0079	0.0096±0.0086	0.0036±0.0011	n.d.	0.0012±0.0011	0.021±0.018
MT	(E)-4,8-Dimethyl-1,3,7-nonatriene	n.d.	0.00063±0.00023	0.00067±0.00045	n.d.	0.022±0.024	0.018±0.025	n.d.
MT	Alloocimene	0.0094±0.0024	0.0055±0.0048	0.00055±0.00024	0.3±0.22	0.00021±0.000094	0.00019±0.000072	0.049±0.051
MT	2,6-Dimethyl-1,3,5,7-octatetraene, E	n.d.	n.d.	0.00020±0.000069	n.d.	0.00019±0.000051	0.00015±0.000023	n.d.
Total Monoterpenes		**3.73±3.74**	**1.64±1.49**	**2.04±1.03**	**2.57±1.75**	**0.067±0.028**	**0.051±0.046**	**5.19±5.09**

Table B.1 Continued

SQ	Copaene	0.00045±0.00034	0.020±0.016	0.00049±0.00016	0.0015±0.00089	0.0089±0.0057	0.0027±0.0014	0.017±0.01
SQ	Beta-cubebene	0.00054±0.00048	0.0017±0.0015	0.00040±0.00021	0.00077±0.00066	0.0044±0.0039	0.00081±0.00059	0.0063±0.0016
SQ	Isolongifolene	0.0043±0.0034	0.015±0.012	0.0031±0.0015	0.015±0.022	0.0016±0.001	0.00049±0.00031	0.016±0.013
SQ	Alpha-cedrene	0.00025±0.00011	0.00041±0.00021	0.00035±0.00024	0.00043±0.00035	0.00035±0.000046	0.00036±0.000064	n.d.
SQ	trans-Caryophyllene	0.0085±0.0069	0.0068±0.0079	0.030±0.035	0.005±0.0049	0.024±0.032	0.012±0.014	0.26±0.052
SQ	Alpha-humulene	0.0023±0.0016	0.0018±0.0024	0.018±0.011	0.00048±0.00033	0.01±0.0079	0.0046±0.0063	0.012±0.0034
SQ	Beta-farnesene	n.d.	0.0025±0.0035	0.0025±0.00097	n.d.	0.0015±0.00043	0.0011±0.00081	n.d.
SQ	Germacrene-D	0.00026±0.00027	0.0021±0.0015	0.00023±0.000035	0.00067±0.00045	0.0068±0.0066	0.0019±0.0021	0.016±0.0039
SQ	Alpha-Bergamotene	n.d.	n.d.	0.00045±0.00021	n.d.	0.00031±0.0001	n.d.	n.d.
SQ	E,E-Alpha-Farnesene	n.d.	n.d.	n.d.	n.d.	n.d.	0.00042±0.0001	n.d.
SQ	Beta-selinene	0.00085±0.00065	0.0016±0.0016	0.0015±0.0015	0.00076±0.00064	n.d.	n.d.	n.d.
SQ	Alpha-muurolene	0.00046±0.00042	0.022±0.017	0.00032±0.00011	0.0017±0.0012	0.0027±0.0026	0.0016±0.001	0.071±0.022
SQ	Gamma-cadinene	0.00042±0.0003	0.027±0.033	0.0006±0.00023	0.0012±0.0011	0.0038±0.0042	0.0022±0.0017	0.066±0.064
SQ	Alpha-cadinene	n.d.	0.00097±0.00089	0.000098±0.000009	n.d.	0.00063±0.00038	0.00051±0.00031	n.d.
-	Cis-Alpha-Bisabolene	0.00019±0.000047	0.0021±0.0033	0.00076±0.00015	n.d.	0.00044±0.00013	0.00037±0.00027	n.d.
Total Sesquiterpenes		**0.012±0.0099**	**0.098±0.083**	**0.042±0.049**	**0.018±0.02**	**0.05±0.043**	**0.023±0.025**	**0.24±0.19**
OX	2-Butanone	n.d.	n.d.	n.d.	0.00021±0.00016	n.d.	n.d.	n.d.
OX	Furan. 2-methyl-	0.00071±0.00046	0.00055±0.00014	0.0032±0.0017	0.0018±0.00091	0.0057±0.0042	0.0052±0.0024	0.0021±0.0014
OX	2-Methyl-3-buten-2-ol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
OX	Crotonaldehyde	0.0082±0.0037	0.0076±0.0050	0.018±0.0059	0.011±0.0076	0.023±0.013	0.017±0.0088	0.0098±0.0018
OX	Butyl aldoxime. 3-methyl-. syn-	n.d.	n.d.	n.d.	n.d.	0.001±0.00038	n.d.	n.d.
OX	Isocineole	n.d.	0.00090±0.00058	0.00057±0.000031	n.d.	n.d.	n.d.	0.00095±0.00026
OX	p-Methylanisole	0.00096±0.00055	n.d.	0.00044±0.00022	n.d.	0.00023±0.00013	n.d.	n.d.
OX	Eucalyptol	0.26±0.19	0.030±0.031	0.34±0.15	0.0026±0.0019	0.015±0.017	0.043±0.031	0.086±0.057

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Table B.1 Continued

OX	1-Octanol	0.017±0.011	0.0041±0.0027	0.0087±0.0032	0.026±0.021	0.002±0.0011	0.0023±0.00021	0.039±0.036
OX	Dihydromyrcenol	0.014±0.0089	0.00055±0.00034	0.0016±0.0012	0.036±0.046	0.00098±0.00017	0.00057±0.00039	0.01±0.0085
OX	Gamma-Terpineol	0.014±0.011	0.015±0.013	0.0096±0.010	0.031±0.0038	0.00089±0.00049	n.d.	0.12±0.062
OX	L-Fenchone	0.0015±0.0018	0.00041±0.00021	0.0014±0.00023	0.00068±0.00073	n.d.	0.00021±0.000068	0.0027±0.0013
OX	Rosefuran	n.d.	n.d.	n.d.	0.003±0.00049	0.00054±0.00024	n.d.	n.d.
OX	Tetrahydrolinalool	n.d.	n.d.	0.00055±0.00026	n.d.	n.d.	n.d.	n.d.
OX	Linalool L	n.d.	0.060±0.056	0.036±0.030	0.032±0.025	0.059±0.06	0.022±0.017	0.067±0.058
OX	D-Fenchyl alcohol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
OX	2-Methyl-6-methylene-1,7-octadien-3-one	0.020±0.021	0.00057±0.00029	0.0022±0.0014	n.d.	n.d.	n.d.	n.d.
OX	2-tert-Butylcyclohexanone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
OX	trans-Dihydro-b-terpineol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
OX	Camphor	0.0077±0.0056	0.0018±0.0023	0.11±0.14	0.0013±0.00089	0.0011±0.00095	0.00095±0.00019	0.0038±0.0034
OX	Isoborneol	0.008±0.0063	0.00024±0.000028	0.020±0.0020	n.d.	0.0025±0.0036	0.0025±0.0026	n.d.
OX	d-Pinocarvone	0.021±0.015	0.0010±0.0011	0.0062±0.0036	0.0074±0.0075	0.0012±0.00066	n.d.	0.005±0.0073
OX	2-(1,1-dimethylethyl)-cyclohexanol	n.d.	n.d.	n.d.	0.0086±0.008	n.d.	n.d.	n.d.
OX	4-Terpineol	0.050±0.043	0.022±0.023	0.019±0.024	n.d.	0.0011±0.001	0.001±0.00073	0.24±0.16
OX	Alpha-Terpineol	0.24±0.20	0.017±0.019	0.043±0.037	0.021±0.014	0.0039±0.0004	0.0036±0.0031	0.08±0.045
Total Oxygenated Compounds		**0.58±0.22**	**0.15±0.14**	**0.59±0.25**	**0.1±0.064**	**0.087±0.052**	**0.074±0.05**	**0.6±0.24**
OX-SQ	Methyl Eugenol	0.00046±0.00049	0.00025±0.000025	0.00016±0.000051	0.0013±0.0002	0.00034±0.00019	0.00024±0.0002	n.d.
OX-SQ	(n.d.)n.d.Spathulenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
OX-SQ	Guaiol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	0.017±0.01
Total Oxygenated Sesquiterpenes		**0.00038±0.00048**	**0.00012±0.00014**	**0.00014±0.000081**	**0.00045±0.0007**	**0.00028±0.00022**	**0.00012±0.00019**	**n.d.**

n.d.: Not detected.

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Table B.2 Raw BVOC emission factors (average±standard deviation) for the trees (µg m^{-2} h^{-1}) under experimental conditions

Group	Compound	Troy Fir	Cilician Fir	Uludag Fir	Boz Pirnal Oak	Ispir Oak	Vulcanic Oak	Oriental Sweetgum
Isoprene	**Isoprene**	**657±579**	**5373±2552**	**682±646**	**13.0±11.7**	**2695±2825**	**1433±1430**	**1773±1663**
MT	Tricyclene	2.62±2.56	0.20±0.093	0.61±0.37	0.39±0.61	0.084±0.075	0.024±0.017	0.051±0.019
MT	Alpha-Pinene	86.6±23.0	184±145	604±439	11.9±2.26	2.89±3.79	2.49±1.66	15.1±16.8
MT	Alpha-Fenchene	1.57±1.73	0.15±0.059	0.20±0.079	0.13±0.019	n.d.	n.d.	0.061±0.0047
MT	Camphene	20.2±13.4	1.13±0.78	9.10±4.39	0.53±0.45	0.31±0.23	0.15±0.13	0.51±0.47
MT	Sabinene	10.5±8.89	4.02±3.60	19.4±4.52	1.56±1.48	1.13±1.45	0.97±0.85	420±377
MT	Beta-Pinene	149±151	294±322	143±95.0	22.5±22.6	0.73±1.10	1.51±1.49	11.0±9.80
MT	Beta-Myrcene	67.1±77.8	48.1±48.1	57.9±70.1	21.2±15.7	0.45±0.27	0.92±1.18	7.33±5.63
MT	l-Phellandrene	4.07±4.33	2.81±1.86	2.35±2.39	n.d.	0.048±0.026	0.026±0.0083	1.64±1.44
MT	Delta 3-Carene	2.27±2.33	0.61±0.33	1.82±1.68	3.42±4.00	0.086±0.079	0.083±0.045	0.11±0.072
MT	Alpha-Terpinene	0.68±0.40	0.75±0.68	1.94±2.20	0.22±0.19	0.086±0.068	0.061±0.069	3.46±3.26
MT	m-Cymene	0.13±0.085	0.057±0.028	0.25±0.17	0.058±0.047	0.047±0.027	0.024±0.021	0.069±0.066
MT	p-isopropyl toluene (p-Cymene)	13.4±8.01	2.15±1.36	7.71±3.96	0.91±0.89	0.79±0.82	0.13±0.075	7.05±3.84
MT	Limonene	515±769	n.d.	130±93.4	19.6±16.8	0.80±0.54	0.41±0.24	10.8±3.94
MT	Beta-Phellandrene	n.d.	110±93.8	n.d.	n.d.	n.d.	n.d.	n.d.
MT	cis-Ocimene	6.03±1.52	6.91±5.80	2.04±0.78	30.8±21.3	0.15±0.12	0.11±0.067	1.26±1.36
MT	trans-beta-Ocimene	0.43±0.15	0.28±0.20	0.71±0.48	604±397	0.73±0.95	0.38±0.45	0.56±0.27
MT	Gamma-Terpinene	2.82±2.85	2.29±1.80	5.35±5.15	0.87±0.59	0.15±0.13	0.067±0.048	7.55±6.71
MT	Terpinolene	2.34±1.23	3.71±2.91	3.57±3.42	1.00±0.34	n.d.	0.15±0.14	1.71±1.46
MT	(E)-4,8-Dimethyl-1,3,7-nonatriene	n.d.	0.28±0.10	0.23±0.15	n.d.	3.10±3.26	2.23±3.02	n.d.
MT	Alloocimene	3.02±0.54	2.28±1.96	0.20±0.090	82.4±61.2	0.031±0.012	0.021±0.0067	3.97±3.98
MT	2,6-Dimethyl-1,3,5,7-octatetraene, E	n.d.	n.d.	0.063±0.013	n.d.	0.029±0.010	0.016±0.0075	n.d.
Total Monoterpenes		**762±746**	**662±592**	**960±586**	**666±451**	**10.5±4.64**	**7.01±7.08**	**409±417**

Table B.2 Continued

SQ	Copaene	0.16±0.13	8.21±6.22	0.17±0.066	0.39±0.23	1.31±0.80	0.33±0.19	1.43±0.81
SQ	Beta-cubebene	0.18±0.15	0.67±0.55	0.14±0.059	0.20±0.18	0.67±0.60	0.096±0.064	0.57±0.049
SQ	Isolongifolene	1.51±1.16	5.98±4.68	1.09±0.54	3.88±5.46	0.23±0.14	0.057±0.036	1.32±1.07
SQ	Alpha-cedrene	0.088±0.016	0.17±0.078	0.13±0.073	0.11±0.096	0.055±0.015	0.043±0.0096	n.d.
SQ	trans-Caryophyllene	2.61±2.01	2.83±3.05	11.5±14.0	1.30±1.28	3.73±4.78	1.44±1.70	21.9±2.37
SQ	Alpha-humulene	0.70±0.44	0.73±0.92	6.97±4.40	0.12±0.077	1.57±1.25	0.54±0.76	0.96±0.25
SQ	Beta-farnesene	n.d.	0.99±1.37	0.96±0.31	n.d.	0.20±0.052	0.13±0.094	n.d.
SQ	Germacrene-D	0.11±0.12	0.82±0.52	0.07±0.022	0.17±0.11	1.10±1.17	0.23±0.25	1.29±0.23
SQ	Alpha-Bergamotene	n.d.	n.d.	0.16±0.086	n.d.	0.047±0.0076	n.d.	n.d.
SQ	E,E-Alpha-Farnesene	n.d.	n.d.	n.d.	n.d.	n.d.	0.053±0.011	n.d.
SQ	Beta-selinene	0.25±0.18	0.62±0.57	0.33±0.28	0.20±0.16	n.d.	n.d.	n.d.
SQ	Alpha-muurolene	0.16±0.15	8.91±6.30	0.11±0.042	0.44±0.32	0.42±0.44	0.19±0.12	5.96±1.97
SQ	Gamma-cadinene	0.15±0.12	10.2±12.1	0.21±0.089	0.32±0.29	0.56±0.58	0.25±0.20	5.56±5.48
SQ	Alpha-cadinene	n.d.	0.37±0.31	0.034±0.0021	n.d.	0.096±0.057	0.061±0.038	n.d.
SQ	Cis-Alpha-Bisabolene	0.067±0.026	0.84±1.27	0.27±0.037	n.d.	0.061±0.016	0.042±0.028	n.d.
Total Sesquiterpenes		**3.9±2.81**	**38.7±30.4**	**15.6±18.8**	**4.77±5.19**	**7.59±6.83**	**2.67±2.97**	**19.9±16.2**
OX	2-Butanone	n.d.	n.d.	n.d.	0.054±0.037	n.d.	n.d.	n.d.
OX	Furan. 2-methyl-	0.21±0.12	0.22±0.034	1.11±0.60	0.47±0.22	0.84±0.62	0.65±0.34	0.17±0.12
OX	2-Methyl-3-buten-2-ol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
OX	Crotonaldehyde	2.64±1.25	2.36±1.00	6.27±1.90	2.85±1.91	3.41±1.81	2.05±1.18	0.83±0.15
OX	Butyl aldoxime. 3-methyl-. syn-	n.d.	n.d.	n.d.	n.d.	0.15±0.058	n.d.	n.d.
OX	Isocineole	n.d.	0.36±0.21	0.21±0.037	n.d.	n.d.	n.d.	0.078±0.022
OX	p-Methylanisole	0.33±0.21	n.d.	0.15±0.075	n.d.	0.034±0.017	n.d.	n.d.
OX	Eucalyptol	81.7±58.7	11.8±12.1	121±55.1	0.69±0.54	2.54±2.91	5.26±3.85	7.03±4.45

Table B.2 Continued

OX	1-Octanol	6.47±5.02	1.65±1.06	3.44±0.85	6.70±5.12	0.32±0.19	0.28±0.013	3.19±2.97
OX	Dihydromyrcenol	4.34±2.42	0.22±0.12	0.55±0.40	9.03±11.7	0.13±0.055	0.068±0.048	0.84±0.70
OX	Gamma-Terpineol	4.73±4.05	5.97±4.69	3.57±3.93	8.60±1.31	0.14±0.097	n.d.	10.3±5.57
OX	L-Fenchone	0.46±0.53	0.16±0.093	0.50±0.043	0.18±0.18	n.d.	0.026±0.0089	0.22±0.11
OX	Rosefuran	n.d.	n.d.	n.d.	0.80±0.15	0.084±0.048	n.d.	n.d.
OX	Tetrahydrolinalool	n.d.	n.d.	0.19±0.084	n.d.	n.d.	n.d.	n.d.
OX	Linalool L	n.d.	23.5±21.7	13.5±11	8.20±6.21	8.31±7.89	2.56±2.00	5.42±4.70
OX	D-Fenchyl alcohol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
OX	2-Methyl-6-methylene-1,7-octadien-3-one	8.00±9.58	0.24±0.11	0.59±0.24	n.d.	n.d.	n.d.	n.d.
OX	2-tert-Butylcyclohexanone	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
OX	trans-Dihydro-b-terpineol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
OX	Camphor	2.40±1.46	0.70±0.95	41.6±50.0	0.46±0.12	0.18±0.17	0.11±0.016	0.31±0.27
OX	Isoborneol	2.24±1.78	0.092±0.015	5.81±1.97	n.d.	0.40±0.61	0.31±0.31	n.d.
OX	d-Pinocarvone	7.20±4.28	0.41±0.42	2.18±1.21	1.92±1.86	0.17±0.10	n.d.	0.41±0.59
OX	2-(1,1-dimethylethyl)-cyclohexanol	n.d.	n.d.	n.d.	2.33±2.13	n.d.	n.d.	n.d.
OX	4-Terpineol	27.9±28.5	9.00±9.24	7.20±9.45	n.d.	0.19±0.18	0.12±0.092	19.7±13.8
OX	Alpha-Terpineol	127±123	6.90±7.32	15.9±14.3	5.50±3.79	0.61±0.024	0.44±0.40	6.49±3.52
Total Oxygenated Compounds		**263±174**	**60.2±53.8**	**211±99**	**26.3±16.9**	**12.9±6.43**	**8.97±6.21**	**49.4±20.3**
OX-SQ	Methyl Eugenol	0.14±0.15	0.11±0.018	0.058±0.019	0.34±0.024	0.052±0.028	0.029±0.025	n.d.
OX-SQ	(n.d.)n.d.Spathulenol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
OX-SQ	Guaiol	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Total Oxygenated Sesquiterpenes		**0.12±0.15**	**0.053±0.059**	**0.048±0.029**	**0.11±0.18**	**0.043±0.033**	**0.014±0.022**	**n.d.**

n.d.: Not detected.

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