Environmental Pollution 183 (2013) 143–150

Contents lists available at SciVerse ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Biogenic volatile organic compounds from the urban forest of the Metropolitan Region, Chile

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ARTICLE INFO

Article history:
Received 20 August 2012
Received in revised form
3 April 2013
Accepted 3 April 2013

Keywords:
BVOCs
Photochemical Ozone Creation Potential
Photochemical Ozone Creation Index
Exotic and native arboreal species
Metropolitan Region
Chile

ABSTRACT

Tropospheric ozone is a secondary pollutant whose primary sources are volatile organic compounds and nitrogen oxides. The national standard is exceeded on a third of summer days in some areas of the Chilean Metropolitan Region (MR). This study reports normalized springtime experimental emissions factors (EF) for biogenic volatile organic compounds from tree species corresponding to approximately 31% of urban trees in the MR. A Photochemical Ozone Creation Index (POCI) was calculated using Photochemical Ozone Creation Potential of quantified terpenes. Ten species, natives and exotics, were analysed using static enclosure technique. Terpene quantification was performed using GC-FID, thermal desorption, cryogenic concentration and automatic injection. Observed EF and POCI values for terpenes from exotic species were 78 times greater than native values; within the same family, exotic EF and POCI values were 28 and 26 times greater than natives. These results support reforestation with native species for improved urban pollution management.

1. Introduction

1.1. General

Tropospheric ozone is a regulated secondary pollutant. Some areas of the Metropolitan Region of Chile (MR) exceeds the national standard of an 8-h mobile average of 120 μg/m^3 N (DS N°112, 2002). During summer months, the national standard is exceeded on a third of all days (Seguel et al., 2012). Central Chile, including the MR, is under the influence of subtropical anticyclone conditions, which frequently lead to clear skies and temperatures that favour evaporative emissions of volatile organic compounds (VOCs) – key ozone precursors – and increase the efficiency of chemical and photochemical reactions involved in ozone formation (Rappenglück et al., 2000; Morales, 2006). The MR (33.5° S, 70.8° W) is a closed basin (450–900 masl) surrounded by mountains with altitudes between 1000 and 5000 masl. This formation limits wind flow and air exchange within the basin where the city of Santiago is located. Wind speed in the city is low, averaging 2.2 m s^{-1}; the predominant direction is SW to NE during the day and the reverse at night. The topography of the basin tends to produce stagnation of the air mass and increases the accumulation of pollutants over the city (Préndez et al., 2011).

In Santiago, high concentrations of ozone during the summer months are a function of the chemical reactions involved in pollutant formation. Nitric oxides (NO_x = NO + NO_2) primarily derived from motor vehicles, anthropogenic and biogenic volatile organic compounds (VOCs), and climatic conditions such as temperature and solar radiation influence these reactions. The ozone–precursor relationship can be understood by a distinction between NO_x-sensitive and VOC-sensitive (or NO_x-saturated) chemical regimes (Sillman, 1999). According to Elshorbany et al. (2009), in summertime atmospheric conditions, photochemical ozone formation in the urban atmosphere of Santiago seems to be VOC-sensitive. In their study, biogenic VOCs and BVOCs were estimated using an emissions inventory in which the emissions factors (EF) were approximated using a taxonomical approach for native trees and values obtained from literature for exotics. Seguel et al. (2012) used a VOCs/NO_x ratio experimentally calculated from the official MR pollution-monitoring network and reached a similar conclusion.

The urban forest provides many direct and indirect ecosystem services. Some of these include: improved human health, community empowerment, climate change mitigation, recreational

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http://dx.doi.org/10.1016/j.envpol.2013.04.003

benefits, wildlife habitat, and aesthetic value (Escobedo et al., 2008). Another potential ecosystem service is the reduction of air pollution, which can be divided into direct and indirect processes. Direct reduction of air pollution occurs when trees capture particulate matter on their leaves or absorb ozone and other gaseous pollutants through their stomata or by the dissolution of contaminants on the moist surfaces of their leaves (Akbari, 2002). Indirect reduction occurs when the lower air temperatures produced by the shading and evapotranspiration of urban trees reduce the rate of photochemical reactions that favour the formation of ozone and other atmospheric secondary pollutants (Nowak et al., 2000). However, trees also emit VOCs and therefore potentially contribute to ozone production in the atmosphere. Calfapietra et al. (2009) found that while BVOCs emissions can protect plants against oxidative stress, they may also substantially alter the O_3 flux between atmosphere and biosphere.

Ozone enters a plant through the stomata, generating various reactive oxygen species (Mauzerall and Wang, 2001; Mills et al., 2011). The most obvious effects of O3 on plants are visible on leaf surfaces (chlorosis, specks, spots and necrosis), but ozone also affects productivity in the long term (WHO, 2000; Faoro, and Iriti, 2009; Günthardt-Georg, and Vollenweider, 2007). In Chile there are not secondary standards except for SO_2 and in a very restricted zone impacted by Cu mining exploitation. As a recommendation is used the AOT40 proposed by the European Union (Paoletti, and Manning, 2007).

The effects of tropospheric ozone on international human health have been studied for over three decades. Level of ozone concentration, period of exposure, and individual sensitivity are the most important factors in determining the magnitude of ozone's effects. Epidemiological studies of time series show small positive associations between daily mortality and ozone levels of 120 $\mu g/m^3$ N (calculated as an 8-h mobile average and independent of the effects of particulate matter). Consequently, the current maximum recommended by the WHO (2011) is an 8-h mobile standard of 100 $\mu g/m^3$ N. A decrease in ozone concentration should directly and positively impact the population's health.

Ozone damages many different types of materials, both functionally and aesthetically, and alone and in combination with other pollutants and environmental factors. Impacts of ozone in isolation from other ambient pollutants are most significant for organic materials (elastomers, cellulose fibre, natural textiles, paints and pigments). Synergistic corrosion due to the presence of other ambient pollutants, specifically sulphur dioxide and nitrogen oxides, and/or environmental factors such as high humidity levels can be observed for a variety of metals (Cu, Zn, Ag, Al, Ni, and Fe) and stone materials (marbles, sandstone, limestone, brick, concrete, and gravel) (Health-Canada and Environment-Canada, 1999; Screpanti and De Marco, 2009).

In the troposphere, primary emitters of VOCs include anthropogenic and biogenic sources (Roukos et al., 2009). BVOCs represent about 80% of total global production of reactive VOCs (Guenther et al., 1995); vegetation represents their main source and produces annual emissions of 1200–1600 Tg C (Bon et al., 2011).

Terpenes emitted by plants, which are usually produced as a defence mechanism against temperature, insects and pests (Kansal, 2009) or as a communication mechanism between plants (Peñuelas and Staudt, 2010), include oxygenated compounds (aldehydes and ketones). These BVOCs are generally unsaturated linear and cyclic compounds dominated by isoprene (molecular formula C_5H_8), hemi-terpene (C_5), and monoterpenes (C_{10}) (IUPAC web page, 2012), and represent a significant fraction of total atmospheric BVOCs. More than 15 monoterpene compounds have been found in vegetable species to date (Sharkey and Yeh, 2001; Arneth et al., 2008).

During the day, terpenes interact with radical •OH, ozone and triplet oxygen ($O(^3P)$). At night, when the effective concentration of •OH is low, and in the case of Santiago where the concentration of ozone is also low (MMA web page, 2012), terpenes interact primarily with nitrate radicals (NO_3•). These reactions affect atmospheric oxidative capacity (Lelieveld et al., 2008) and the production of secondary organic aerosols (SOA) (Kroll et al., 2006).

Pacífico et al. (2009) and Peñuelas and Staudt (2010) studied the influence of BVOCs on climate change. A future increase of 2–3 °C in mean global temperature could increase global emissions of BVOCs, which is predicted to occur early this century (IPCC, 2007), and would thereby increase tropospheric ozone and methane, and modify the oxidation capacity of the atmosphere (Liakakoua et al., 2007; Lelieveld et al., 2008). Nevertheless, according to Pacífico et al. (2009), although atmospheric CO_2 stimulate photosynthesis, isoprene emission appears to be inhibited at elevated CO_2 concentrations and enhanced at low CO_2 conditions. Monoterpene emissions are also likely to be influenced by CO2, but there is less experimental evidence than for isoprene (Fowler et al., 2009).

In higher plants it is estimated that between 0 and 10–20% of carbon fixed by photosynthesis ends up as BVOCs, and that physical-chemical factors such as volatility and the rate of compound diffusion may limit the release of synthesized BVOCs from plants' leaves (Fowler et al., 2009). At 30 °C, between 0.5 and 2% of fixed carbon is emitted as isoprene (Niinemets et al., 2004; Nagegowda, 2010), which is not usually stored in leaves (Fall, 1999); however, in many plants, mono and sesqui-terpenes accumulate temporarily in specialized structures after production and prior to volatilization (Papiez et al., 2009). Photosynthetically active radiation (PAR) and temperature are major environmental controllers of terpene emission; temperature influences enzyme activity (isoprene synthase and monoterpene synthases), and also affects the evaporation and diffusion of mono and sesqui-terpenes from plants' storage structures (Fowler et al., 2009). These factors all affect the final production of terpenes. Loreto and Schnitzler (2010) report that an increase in temperature increases BVOCs emission from the large storage structures present in some tree species. Isoprene emissions are dependent upon photosynthetically active radiation, while those of monoterpenes and other hydrocarbons can be emitted day and night (Owen et al., 2002; Pacífico et al., 2009). In order to compare results from different authors, it is necessary to normalize experimental emissions with standard values for PAR and temperature (1000 $\mu mol^*m^{-2}*s^{-1}$ and 30 °C, respectively).

An important consideration in the photochemical formation of ozone is that each VOC, anthropogenic or biogenic, presents different reactivity and susceptibility to ozone formation as a consequence of intrinsic chemical behaviour (Derwent et al., 2007b). The propensity to form ozone is known as Photochemical Ozone Creation Potential (POCP).

Each tree emits a different mixture of BVOCs, and potential to form ozone therefore depends on the sum of the EF of each of the chemicals emitted. The photochemical ozone formation from NO_x and BVOCs should vary according to the set of terpenes involved and their different reactivity with various chemical species present in the atmosphere (Derwent et al., 2007a). POCP describes relative reactivity of the compounds in the atmosphere (mainly with •OH), and therefore is not an absolute measure of ozone productivity (Derwent et al., 2007b).

In order to calculate the environmental impact of the tree species studied on ozone formation, it was necessary to relate the chemical reactivity of organic compounds to the tree species emissions. To do so, we developed an index that accounts for both aspects: the Photochemical Ozone Creation Index (POCI), which allows for the ranking of tree species according to their potential

impact on ozone formation. This index does not represent any absolute measure of ozone productivity.

2. Materials and method

2.1. Sampling and chemical analysis

Six exotic tree species: *Prunus cerasifera* (PC), *Prunus cerasifera var. nigra Pissadii* (PCVNP), *Robinia pseudoacacia* (RP), *Acacia dealbata* (AD), *Betula pendula* (BP), and *Olea europaea* (OE), and four native species: *Acacia caven* (AC), *Cryptocarya alba* (CA), *Schinus molle* (SM), and *Maytenus boaria* (MB) were selected. These tree species represent approximately 31% of urban trees in the MR, and are those found on the North Campus of the Universidad de Chile (33.5° Lat S y 70.6° Long W), Santiago, MR, at approximately 500 masl. Table 1 shows PAR, temperature and relative humidity during the sampling period (austral spring). Species were sampled in the order indicated by Table 1. Greatest variability is observed in PAR for all species, though higher PAR readings do not necessarily correspond to the highest temperatures. Average temperature was approximately 28 °C, with an average relative humidity of 60%.

Selected sun-exposed branches were visually healthy with no evidence of herbivory, pests, or disease, and were representative of sampled species (Simon et al., 2005; Padhy and Varshney, 2005; Moukhtar et al., 2006). Measurements were repeated within the same branch to reduce sample variability (Tsui et al., 2009). Using static enclosure technique, five measurements (absorption of chemicals in Tenax tubes (Arnts, 2010), temperature, PAR and relative humidity measured in a chamber at five minute intervals) were performed daily (9:00, 11:00, 13:00, 15:00 and 17:00 h local time), half an hour each, for 5 days, for each tree species. At the end of the experiment the branches were cut and oven-dried at a temperature of 60 °C (WTB-Binder) to perform biomass calculation. In order to avoid chemical losses, quantification of BVOCs using GC-FID was performed immediately after sampling (Préndez and Peralta, 2005). Calibration curves were used from Sigma Aldrich certified standards for isoprene, 15 monoterpenes, and a sesquiterpene. Detection and quantification limits were calculated as 3 and 10 times the standard deviation, respectively.

2.2. Data processing

The concentrations obtained for each chemical species (isoprene, α-pinene, β-mircene, (−)-camphene, 2-carene, 3-carene, α-terpinene, limonene, cineole, γ-terpinene, linalool, mentol, terpineol, DL citronellol, carvacrol, and trans-caryophyllene) were used to calculate BVOCs emission factors (EF) using the mathematical expression

$$EF = \frac{(C^{*}Q)}{M} \quad (1)$$

where

EF: Emission factor, expressed in μg g_{ldw}^{-1} h^{-1}
C: Compound concentration, expressed in μg m^{-3}
Q: Sampled air flow, expressed in m^3 h^{-1}
M: Mass of dry biomass, expressed in grams of leaf dry weight (ldw)

Standardization of values for each terpene at each sampled time was performed using the algorithms proposed by Guenther et al. (1993) at 30 °C and 1000 μmol m^{-2} s^{-1}. All results reported in this work correspond to the arithmetic mean of the 25 values collected. Standard deviation (s) was calculated using Eq. (2), commonly referred to as population standard deviation because environmental variables do not necessarily follow normal distribution.

Table 1
Mean value, and corresponding standard deviation for studied tree species.

Species	PAR (μmol m^{-2} s^{-1})	T (°C)	RH (%)
Exotics			
Olea europaea	319 ± 307	23.0 ± 2.6	43.4 ± 4.6
Acacia dealbata	337 ± 369	18.0 ± 3.3	76.2 ± 5.0
Betula pendula	580 ± 599	22.9 ± 2.0	64.2 ± 1.7
Prunus cerasifera	853 ± 513	32.9 ± 5.8	66.6 ± 5.1
Prunus cerasifera var. Nigra Pissardii	965 ± 671	36.3 ± 8.8	55.7 ± 6.3
Robinia pseudoacacia	843 ± 294	31.9 ± 3.0	54.9 ± 7.0
Natives			
Cryptocarya alba	1228 ± 720	27.8 ± 5.1	58.4 ± 5.0
Schinus molle	1426 ± 807	30.0 ± 6.4	60.0 ± 3.8
Acacia caven	982 ± 228	31.3 ± 4.5	54.8 ± 5.0
Maytenus boaria	742 ± 528	29.5 ± 4.6	66.5 ± 8.3

$$s = \sqrt{\frac{\sum (X - \overline{X})^2}{n}} \quad (2)$$

where

n = Number of samples (25)
$\overline{X}$ = Mean arithmetic value
X = Corresponding individual value

A preliminary POCI was calculated for each tree species according to Eq. (3). This formula incorporates the magnitude of partial emissions for each chemical species based on the experimental EF determined for the Metropolitan Region and on corresponding Photochemical Ozone Creation Potential:

$$POCI = \sum (EF_i{}^{*}POCP_i) \quad (3)$$

where:

EF_i = Emission factors obtained experimentally for each BVOC chemical species
$POCP_i$ = Photochemical Ozone Creation Potential calculated for each BVOC chemical species based on Derwent, 2011 (Personal communication)

Simple correlations were performed to evaluate the relationship between the concentrations of each chemical species emitted by sampled trees and the environmental conditions PAR, relative humidity and temperature measured during each daily sampling (within the enclosure).

Normality was evaluated using Shapiro–Wilk test. In these cases differences in environmental conditions or in EF between native and exotic species were analysed using t-student test, considering grouping (i.e. native or exotic) as a fixed effects factor, with 4 and 6 replicates for native and exotic species, respectively. When no normality was found a Wilcox test was used (R Core Team., 2013; Park, 2009; Quinn and Keough, 2002; Zar, 1999).

3. Results and discussion

Correlations between the concentrations of each chemical species emitted by the sampled trees and the environmental conditions were tested. Different situations were observed. For instance all arboreal species except *Robinia pseudoacacia* show no statistical significant correlation (≥95%) between isoprene and temperature or PAR. *Robinia pseudoacacia* shows $r = 0.946$ between isoprene and PAR, but no correlation with temperature. Similarly, different situations were observed between the different monoterpene and temperature or PAR. For instance, 2-carene, α-terpinene, limonene concentrations show a statistical significance correlation with temperature or PAR in *Prunus cerasifera, and Prunus cerasifera var. nigra Pissadii*, but not in *Robinia pseudoacacia*, *Cryptocarya alba, and Schinus molle.* No statistical significant differences were observed between the exotics and the native species (as two groups) and the environmental conditions, using t-student test showed in Table 1.

3.1. EF of isoprene

No statistical significant differences (t-student test) were observed in the normalized mean values and standard deviations of isoprene EF between the exotics and the native species as two groups (Fig. 1). Isoprene represents 57% and 99% of total emissions by mass of exotic and native species, respectively, with the exception of *Betula pendula,* where the highest percentage of emissions corresponds to monoterpenes and trans-caryophyllene (70%).

The difference between the EF of exotic and native species was statistically significant ($p < 0.05$). *Schinus molle*, has EF slightly higher than those of *Prunus cerasifera* and *Olea europaea*. *Maytenus boaria* had the lowest isoprene emissions. The EF for isoprene of *Schinus molle* demonstrates a large standard deviation because EF at 9:00 and 17:00 h are very high compared to EF for the rest of the day (Table 2). For isoprene emitted from *Prunus cerasifera* and *Prunus cerasifera var. nigra Pissardii*, a significant variability between morning and afternoon EF can also be observed. Mean daily EF for certain species may introduce a course bias in the calculation

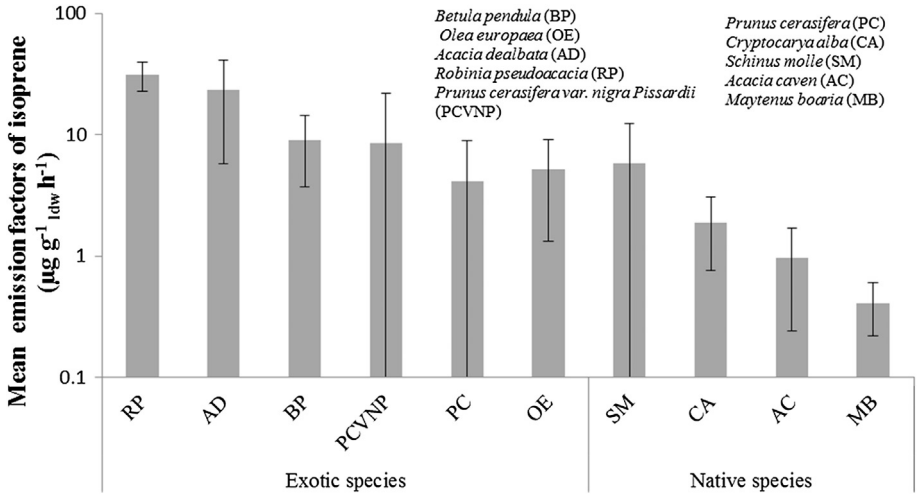

Fig. 1. Standard emission factors for total isoprene for exotic and native species of urban trees in Santiago, expressed in μg g_{ldw}^{-1} h^{-1}.

of ozone forming potential, which might determine one EF for the morning (9:00 and 11:00 h) and another for the afternoon (13:00 to 17:00 h) for *Acacia dealbata*, *Prunus cerasifera var. Pissardii nigra*, *Olea europaea*, and *Prunus cerasifera*.

Robinia pseudoacacia shows the highest EF for isoprene, with values between 20.7 and 44.7 μg g_{ldw}^{-1} h^{-1}. A comparison between isoprene EF for *Robinia pseudoacacia* calculated in this work and those reported by different authors using different methods is shown in Table 3. The value reported by this investigation is approximately 2.8 times greater than that reported by Benjamin et al. (1996), Lamb et al. (1983) and Winer et al. (1983) all of whom used similar techniques. The EF results of this investigation are approximately twice as great as those derived by Guenther et al. (1994) who used a different technique. However, the EF obtained by this study is much smaller (4–7 times so) than that observed by Geron et al. (2001) or Guenther et al. (1996). Clearly, varying technique affects EF values. Nevertheless, differences observed while using the same technique may be attributable to environmental conditions. *Robinia pseudoacacia* is an exotic species in Chile and may employ adaptation mechanisms to survive, one of which could result in the increase of isoprene emissions.

3.2. EF of monoterpenes and trans-caryophyllene

Tables 4a and b show maximum and minimum experimentally determined EF values for each monoterpene and trans-

Table 2
Mean isoprene emission factors and standard deviation for standard conditions from native and exotic tree species, expressed as μg g_{ldw}^{-1} h^{-1}.

Species	Local time				
	9:00	11:00	13:00	15:00	17:00
Cryptocarya alba	4.06 ± 0.44	1.96 ± 0.12	1.37 ± 0.09	0.95 ± 0.03	1.05 ± 0.06
Schinus molle	14.4 ± 24.5	0.45 ± 0.46	0.79 ± 1.11	0.21 ± 0.18	13.3 ± 6.9
Acacia caven	0.84 ± 0.65	0.29 ± 0.23	0.26 ± 0.18	1.89 ± 1.16	2.28 ± 0.83
Maytenus boaria	0.71 ± 0.20	0.49 ± 0.13	0.22 ± 0.07	0.19 ± 0.02	0.45 ± 0.22
Betula pendula	6.73 ± 2.77	3.09 ± 0.96	5.84 ± 2.89	10.6 ± 5.56	18.6 ± 4.85
Olea europaea	3.28 ± 3.51	0.91 ± 0.81	6.00 ± 3.46	6.46 ± 2.17	10.71 ± 1.2
Acacia dealbata	2.31 ± 1.52	6.31 ± 4.15	21.6 ± 14.0	46.0 ± 30.3	42.1 ± 24.5
Prunus cerasifera	13.2 ± 10.8	4.77 ± 0.98	1.04 ± 0.11	0.74 ± 0.20	0.63 ± 0.13
Prunus cerasifera var. nigra Pissardii	35.5 ± 10.7	5.13 ± 0.36	0.66 ± 0.07	0.65 ± 0.09	0.55 ± 0.07
Robinia pseudoacacia	37.0 ± 13.7	24.4 ± 15.2	44.7 ± 20.6	29.7 ± 10.1	20.7 ± 6.2

Table 3
Isoprene emission factors from *Robinia pseudoacacia* determined in Chile and in the United States by previous investigations, expressed as μgC g_{ldw}^{-1} h^{-1} and μg g_{ldw}^{-1} h^{-1}.

Species	This study	Geron et al. (2001)	Benjamin et al. (1996)	Guenther et al. (1996)	Guenther et al. (1994)	Lamb et al. (1983)	Winer et al. (1983)
μg g_{ldw}^{-1} h^{-1}	31.3	171.13	11.8[b]	133.73–217.6	15.87	13.5[b]	11[b]
μgC g_{ldw}^{-1} h^{-1}	27.6	151[b]	10.41	118–192[b]	14[b]	11.91	9.71
Site of sampling	Chile, MR[a] (exotic)	California (native)	California (native)	California (native)	California (native)	Not mentioned	California (native)
Sampling technique	Static enclosure	Foliar density with land use coverage from the Geoecology Database	Compilation of species studied	Not mentioned	Species composition and foliar mass data	Enclosure and micrometeorological	Enclose a vegetative simple, a single branch or several small branches

[a] MR: Metropolitan Region.
[b] Data in the original paper.

Table 4a
Maximum and minimum terpene emission factors from four native species under standard conditions (μg g_{ldw}^{-1} h^{-1}).

Terpenes	*Cryptocarya alba*	*Schinus molle*	*Acacia caven*	*Maytenus boaria*
α-Pinene	0.03–0.01	0.00	ND[a]	ND
β-Mircene	0.00	0.00	0.00	ND
(−)Camphene	ND	0.01–0.00	ND	ND
2-Carene	ND	0.00	0.01–0	ND
3-Carene	ND	ND	ND	0.00-
α-Terpinene	ND	ND	ND	ND
Limonene	0.02–0.01	0.02–0.01	0.00	0.00
Cineole	0.08–0.05	0.01–0.01	0–00	0.02–0.01
γ-Terpinene	0.00	ND	ND	ND
Linalool	0.03–0.02	0.02–0.00	0.00	0.01–0.00
Mentol	ND	ND	ND	ND
Terpineol	ND	ND	ND	ND
DL citronellol	ND	ND	ND	ND
Carvacrol	ND	ND	ND	ND
Trans-caryophyllene	ND	ND	ND	ND

[a] ND = Not determined because concentrations were under quantification limits.

caryophyllene from different tree species in Santiago: natives (Table 4a), and *exotics* (Table 4b).

Exotic species emit a greater number of monoterpenes (13) than natives (9), sometimes by an order of magnitude of 1:3. Especially important are the differences for cineole and (−) camphene. In all tree species, the principal monoterpene was cineole, as similarly reported for *Quercus ilex* in Rome (Kesselmeier et al., 1996). Kegge and Pierik (2010) suggest that cineole, like the (−)-camphene, inhibits germination and plant growth. It has also been observed that cineole concentrations increase in ozone enriched atmospheres, while β-myrcene concentrations decrease to as low as zero (Pinto et al., 2007). In this study, the concentrations of β-myrcene were very low for native trees and nonexistent for exotics. In Santiago, high cineole emissions by exotic species, specifically in the case of *Betula pendula* (EF 11.7 μg g_{ldw}^{-1} h^{-1}), could in theory produce a positive feedback effect of ozone production, although the contribution to ozone formation by cineole emissions ($POCP_i = 75$, Table 5) is lower than that of other monoterpenes (such as α-terpinene, which is emitted in low concentrations). This behaviour may be due to the low reactivity of certain compounds present in the atmosphere, as shown in Table 5; α-terpinene is observed in the emissions of *Prunus cerasifera*, *Prunus cerasifera var. Pissardii nigra*, and *Robinia pseudoacacia*, but not those of native species, and this compound has the greatest potential for ozone formation ($POCP_i = 150$).

Table 5
Half-lives of various terpenes undergoing reactions with O_3 and •OH and $•NO_3$ radicals and the Photochemical Ozone Creation Potential (POCP) calculated for •OH reaction.

Compound	Lifetime for the reaction[a] with			$POCP_i$[b]
	•OH	O_3	$•NO_3$	
Cineole	1.0 days	>110 days	1.5 years	75
α-Terpinene	23 min	1 min	0.5 min	150
Linalool	52 min	55 min	6 min	100
Limonene	49 min	2.0 h	5 min	71
Camphene	2.6 h	18 days	1.7 days	7
Isoprene	1.4 h	1.3 days	1.6 days	114

[a] Atkinson and Arey (2003).
[b] Derwent, 2011 (personal communication).

Ambient atmospheric concentrations of different compounds are variable, and as a result the instantaneous lifetimes of BVOCs with •OH, $•NO_3$ and O_3 depend on time of day, season, latitude, cloud cover, and the chemical composition of the surrounding air mass (Atkinson and Arey, 2003). Table 5 reflects an approximation of α-terpinene and other terpenes half-lifes in the presence of •OH, $•NO_3$ and O_3 radicals and includes $POCP_i$ as calculated by Derwent in the ambient conditions of England. The real impact of ozone formation by cineole, isoprene or linalool ($POCP_i$ 75, 114 and 100, respectively) could be assessed when chemical and physical atmospheric conditions can be evaluated. Nevertheless, exotic trees under the same conditions are greater emitters of these and others chemical compounds than native trees, and therefore may generate more ozone.

Statistical significant differences (Wilcox test) were observed in the standard mean values and standard deviations of monoterpenes and trans-caryophyllene EF between the exotics and the native species (Fig. 2). These results clearly demonstrate higher values for exotic species than native species; *Betula pendula* demonstrates the highest EF, which corresponds to $1.63^{*}10^{3}$ times that of *Acacia caven*.

Table 6 presents a comparison between the EF for monoterpenes observed in Santiago and those reported by relevant literature for various exotic species in Chile. EF from *Betula pendula* determined in Santiago (using the same technique) are between 200 (0.19 μg g_{ldw}^{-1} h^{-1}, König et al., 1995) to 5 times (5.4 μg g_{ldw}^{-1} h^{-1}, Hakola et al., 1998) higher than those reported in the Northern Hemisphere. Only in the case of the EF for monoterpenes observed for *Robinia pseudoacacia* are the values obtained in Santiago smaller than those reported in referenced literature.

Table 4b
Maximum and minimum terpenes emission factors from six exotic species under standard conditions (μg g_{ldw}^{-1} h^{-1}).

Terpenes	*Betula pendula*	*Olea europaea*	*Acacia dealbata*	*Prunus cerasifera*	*Prunus cerasifera var. nigra Pissardii*	*Robinia pseudoacacia*
α-Pinene	0.16–0.07	0.02–0.01	0.03–0.02	0.04–0	0.03–0	0.04–0
β-Mircene	ND[a]	ND	ND	ND	ND	ND
(−)Camphene	11.10–4.54	1.18–0.68	0.66–0.48	0.00–0	0.00–0	ND
2-Carene	0.147–0.074	0.042–0.025	0.113–0.054	0.182–0.062	0.311–0.087	0.339–0.168
3-Carene	0.03–0.01	0.02–0.01	0.16–0.02	0.09–0.03	0.18–0.06	0.23–0.05
α-Terpinene	ND	ND	ND	0.11–0.05	0.16–0.06	0.14–0.08
Limonene	0.27–0.12	0.07–0.03	0.06–0.03	0.11–0.03	0.07–0.02	0.07–0.02
Cineole	11.70–4.49	2.07–1.20	1.80–0.91	0.31–0.13	0.60–0.19	0.64–0.29
γ-Terpinene	1.75–0.52	1.32–0.55	0.90–0.36	0.06–0.03	0.10–0.04	0.14–0.05
Linalool	2.96–1.23	0.02–0.01	0.04–0.03	0.23–0.14	0.46–0.18	0.56–0.22
Mentol	ND	ND	ND	0.30–0.17	0.52–0.21	0.37–0.19
Terpineol	0.81–0.63	0.29–0.13	0.34–0.26	0.21–0.11	0.32–0.12	0.25–0.13
DL citronellol	ND	ND	ND	0.06–0.03	0.11–0.04	0.11–0.03
Carvacrol	0.48–0.34	ND	0.47–0.00	0.06–0.03	0.12–0.04	0.12–0.06
Trans-caryophyllene	ND	ND	ND	0.03–0.01	0.037–0.022	0.03–0.01

[a] ND = Not determined because concentrations were under quantification limits.

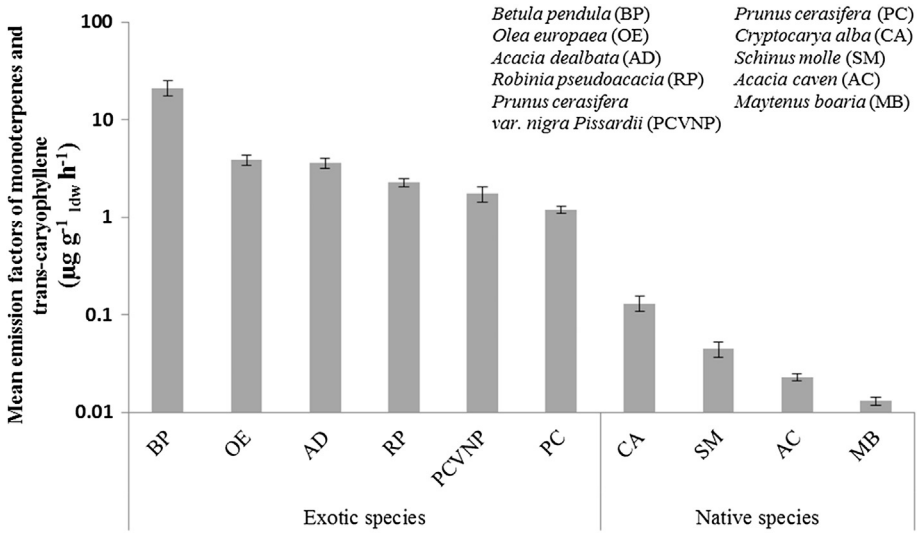

Fig. 2. Mean emission factors and standard deviation for standard conditions of monoterpenes and trans-caryophyllene in μg g^{-1}_{ldw} h^{-1}.

It is important to note that Kesselmeier and Staudt (1999) report a value of 3.7 μg g^{-1}_{ldw} h^{-1} for monoterpenes from *Schinus molle* (California pepper) – much higher than the 0.05 μg g^{-1}_{ldw} h^{-1} reported in this work for *Schinus molle* (considered a native species in Chile).

3.3. Photochemical Ozone Creation Index (POCI)

Table 7 shows total EF and corresponding POCI values for exotic and native species and percentages of relative abundance for each species within the urban forest of Santiago. Results were presented separately when significant variations in emissions were observed throughout the day. In general, native species demonstrate a lower POCI than exotic species. It is clear that *Robinia pseudoacacia* presents the highest EF, POCI, and abundance in Santiago and therefore represents a possibly significant source of tropospheric ozone in the city. This species is native to the Appalachian Mountains on the west coast of the United States (Call and Nilsen, 2003). *Acacia dealbata* demonstrates highest EF in the afternoon, and its high POCI may contribute to ozone formation during these hours; however, its relative abundance in the urban forest is comparatively low. Eight trees show a direct relationship between EF and POCI; *Betula pendula* and *Acacia dealbata* do not present this relationship. *Betula pendula* has a greater EF (daily mean) but lower POCI than *Acacia dealbata*. This difference is due to the differing compositions of their emissions; *Betula pendula* emissions are 70% and 30% isoprene (POCI = 1036) and monoterpenes (POCI = 975), respectively, while *Acacia dealbata* emissions are 14% and 86% isoprene (POCI = 2696) and monoterpenes (POCI = 224), respectively. Additionally, the composition of emissions from different monoterpenes and $POCP_i$ present significant variation. *Acacia dealbata* shows its highest EF and highest isoprene emissions in the afternoon.

Betula pendula, Acacia dealbata and *Olea europaea* present high EF of BVOCs and additionally are strong allergens. The pollen of *Betula pendula* has been identified as the principal allergen in northern Europe, North America, East Asia, northwest Africa and parts of Australia, and causes reactions of the mucosa of the upper aero-digestive tract (sneezing and angioedema) (Viñas, 2002).

According to Hernández et al. (2002), the *Olea europaea* produces one of the most characteristic pollen allergens in Europe and represents an important inducer of allergic diseases within the entire Mediterranean basin; it is responsible for up to 65% of sensitizations.

Table 6
Emission factors for standard conditions of monoterpenes from *Robinia pseudoacacia*, *Betula pendula*, *Olea europaea* and *Prunus cerasifera*, expressed as μg g^{-1}_{ldw} h^{-1}, reported by different researchers.

Species	This work	Literature	Predominant technique	References
Robinia pseudoacacia	2.3	4.7	Enclosure	Lamb et al., 1983
Betula pendula	21.1	0.19	Enclosure	König et al., 1995
		5.4		Hakola et al., 1998
Olea europaea	3.9	0.5	Enclosure	Winer et al., 1983
		0.1		Winer et al., 1992
				Arey et al., 1991
Prunus cerasifera	1.2	0.1	Taxonomic approach	Benjamin et al., 1996

Table 7
Total Mean Emission Factors and standard deviation, Photochemical Ozone Creation Index and relative abundance of exotic and native urban trees species in the Metropolitan Region, Santiago.

Species	Total EF[a] (μg g^{-1}_{ldw} h^{-1})	POCI[b]	Relative abundance (%)
Robinia pseudoacacia	33.6 ± 8.0 [d][c]	3734 [d]	14.4
Prunus cerasifera var. nigra Pissardii	10.3 ± 13.6 [d]	1089 [d]	3.5
	22.0 ± 15.2 [m][d]	2494 [m]	
Prunus cerasifera	5.3 ± 4.8 [d]	548 [d]	5.1
	2.36 ± 0.3 [a][e]	152 [a]	
Betula pendula	30.2 ± 6.6 [d]	2010 [d]	NI[f]
	10.2 ± 4.2 [m]	1146 [m]	
	2.0 ± 0.2 [a]	150 [a]	
Acacia dealbata	27.2 ± 17.9 [d]	2920 [d]	1.2
	7.9 ± 1.9 [m]	763 [m]	
	40.1 ± 13.1 [a]	4357 [a]	
Olea europaea	9.1 ± 3.9 [d]	847 [d]	0.5
	5.3 ± 1.0 [m]	450 [m]	
	11.6 ± 3.6 [a]	1112 [a]	
Schinus molle	5.8 ± 6.4 [d]	660 [d]	1.2
Cryptocarya alba	2.01 ± 1.1 [d]	222 [d]	NI
Acacia caven	0.98 ± 0.7 [d]	111 [d]	5
Maytenus boaria	0.43 ± 0.2 [d]	48 [d]	NI

[a] EF = Emission Factors.
[b] POCI = Photochemical Ozone Creation Index.
[c] d = day.
[d] m = morning.
[e] a = afternoon.
[f] NI = No information.

Prunus cerasifera and *Prunus cerasifera var. Pissardii nigra* (natives to northern Asia) present similar emissions in Santiago at certain hours of the day; however, their EF and POCI values differ significantly. Isoprene emissions and POCI from *Prunus cerasifera var. nigra Pissardii* are double those of *Prunus cerasifera*. Using taxonomic studies, Benjamin et al. (1996) determined that *Prunus cerasifera* emits small quantities of monoterpenes but not isoprene (Table 6) under the environmental conditions of California.

None of the native species studied in this work are allergenic.

4. Conclusions

In Santiago, the principal BVOC emitted by studied tree species is isoprene. Exotic species present emission factors up to 8 times greater than those of native species, and the Photochemical Ozone Creation Index for exotics is approximately five times higher than that of native species. Exotic species represent almost 25% of the relative abundance of the urban forest, and a replacement of these species for native ones could produce a significant reduction of BVOCs emissions to the city's atmosphere, and therefore effectively contribute to a decrease in ozone concentration and the improvement of Santiago's air quality.

Robinia pseudoacacia accounts for more than 14% of the trees of the Metropolitan Region, is a significant source of volatile compounds with the highest POCI of studied trees, and as a result represents the principal source of tropospheric ozone through BVOCs.

Furthermore, the exotic species *Betula pendula*, *Acacia dealbata* and *Olea europaea*, correspond to up to 2% of relative abundance and produce allergens and resultant health problems (Motta et al., 2006; D'Amato, 2002), which are exacerbated by the oxidative atmosphere produced by ozone levels that frequently exceed national standards.

On the other hand, all native species studied are evergreen, a characteristic which contributes to year-round capture of particulate matter, especially during autumn and winter – the period when particulate matter represents the primary contaminant in Santiago and frequently exceeds national regulations (Préndez et al., 2011). In contrast, exotic species are deciduous and do less to mitigate this pollution problem. The loss of leaves during autumn and winter period corresponds to the rainy season and provokes obstruction of sewage and resultant flooding of streets and low-level passages.

Differences in EF observed between *Prunus cerasifera* (5.3 ± 4.8 μg g_{ldw}^{-1} h^{-1}) and *Prunus cerasifera var. Pissardii* nigra (10.3 ± 13.6 μg g_{ldw}^{-1} h^{-1}) (which correspond to the same genus), and between *Acacia caven* (0.98 ± 0.7 μg g_{ldw}^{-1} h^{-1}) and *Acacia* dealbata (27.2 ± 17.9 μg g_{ldw}^{-1} h^{-1}) (which correspond to the same family) indicate that the approximation of EF for BVOCs using a taxonomic method is not appropriate for emissions inventory. Accurate EF values for the urban forest of Santiago will contribute to an improved emissions inventory and as a result improve models and strategies for use in air quality management. The EF used in the official inventory (CONAMA, 1997) considers EF at a level of taxonomical family approximation without distinction between genus (EF for *Prunus* is 42.5 μg g_{ldw}^{-1} h^{-1}; EF for Acacias is 5950 μg g_{ldw}^{-1} h^{-1}), and it is possible that the replacement of the taxonomical approach with an experimental one may result in a drastic decrease of modelled BVOCs emissions.

Emission factors presented in this work were standardized (1000 μmol*m^{-2}*s^{-1} and 30 °C) to allow comparison with the results of other investigations, despite a lack of any clearly observed relationship between concentrations of the terpenes emitted and PAR, temperature and relative humidity.

Further studies of EF for other exotic and native species and during other seasons are under way. New projects will be initiated in order to clarify chemical, taxonomical, biochemical and practical aspects related to the management of the urban forest.

Acknowledgements

Authors acknowledge CENMA (Environmental National Centre), Chile, for its financial support, Dr. Richard Derwent from the Centre for Environmental Policy for his contribution of invaluable POCP data and Dr. Alex Guenther from University Corporation for Atmospheric Research for his continuous encouragement. The authors also thank the anonymous reviewers for their valuable comments and suggestions, all of which have certainly contributed to the improvement of this work.

References

Akbari, H., 2002. Shade trees reduce building energy use and CO2 emissions from power plants. Environmental Pollution 11, S119–S126.

Arey, J., Winer, A.M., Atkinson, R., Aschmann, S.M., Long, W.D., Morrison, C.L., Olszyk, D.M., 1991. Terpenes emitted from agricultural species found in California's central valley. Journal of Geophysical Research 96 (D5), 9329–9336.

Arneth, A., Monson, R.K., Schurgers, G., Niinemets, U., Palmer, P.I., 2008. Why are estimates of global terrestrial isoprene emissions so similar (and why is this not so for monoterpenes)? Atmospheric Chemistry and Physics 8, 4605–4620.

Arnts, R., 2010. Evaluation of adsorbent sampling tube materials and Tenax-TA for analysis of volatile biogenic organic compounds. Atmospheric Environment 44, 1579–1584.

Atkinson, R., Arey, J., 2003. Gas-phase tropospheric chemistry of biogenic volatile organic compounds: a review. Atmospheric Environment 37 (Suppl. No. 2), S197–S219.

Benjamin, M.T., Sudol, M., Bloch, L., Winer, A.M., 1996. Low-emitting urban forests: a taxonomic methodology for assigning isoprene and monoterpene emission rates. Atmospheric Environment 30, 1437–1452.

Bon, D., Ulbrich, I., Gouw, J., Warneke, C., Kuster, W., Alexander, M., Baker, A., Beyersdorf, A., Blake, D., Fall, R., Jimenez, J., Herndon, S., Huey, L., Knighton, W.B., Ortega, J., Springston, S., Vargas, O., 2011. Measurements of volatile organic compounds at a suburban ground site (T1) in Mexico City during the MILAGRO 2006 campaign: measurement comparison, emission ratios, and source attribution. Atmospheric Chemistry and Physics 11, 2399–2421.

Calfapietra, C., Fares, S., Loreto, F., 2009. Volatile organic compounds from Italian vegetation and their interaction with ozone. Environmental Pollution 157, 1478–1486.

Call, L.J., Nilsen, E.T., 2003. Analysis of spatial patterns and spatial association between the invasive tree-of-heaven (*Ailanthus altissima*) and the native black locust (*Robinia pseudoacacia*). The American Midland Naturalist 150 (1), 1–14.

CONAMA (Comisión Nacional del Medioambiente), 1997. Inventario de Emisiones Atmosféricas de la Región Metropolitana para 1997 y Proyecciones al 2005. Elaborado por CENMA. Centro Nacional del Medioambiente.

D'Amato, G., 2002. Environmental urban factors (air pollution and allergens) and the rising trends in allergic respiratory diseases. Allergy 57 (Suppl. 72), 30–33.

Derwent, R.G., Jenkin, M.E., Passant, N.R., Pilling, M.J., 2007a. Reactivity-based strategies for photochemical ozone control in Europe. Environmental Science & Policy 10, 445–453.

Derwent, R.G., Jenkin, M.E., Passant, N.R., Pilling, M.J., 2007b. Photochemical ozone creation potentials (POCPs) for different emission sources of organic compounds under European conditions estimated with a Master Chemical Mechanism. Atmospheric Environment 41, 2570–2579.

DS 112/02 Decreto Supremo Ministerio Secretaría General de la Presidencia de la República. Chile, 2002. Norma de Calidad Primaria de Aire para Ozono.

Elshorbany, Y., Kleffmann, J., Kurtenbach, R., Rubio, M., Lissi, E., Villena, G., Gramsch, E., Rickard, A., Pilling, M., Wiesen, P., 2009. Summertime photochemical ozone formation in Santiago, Chile. Atmospheric Environment 43, 6398–6407.

Escobedo, F., Wagner, J., Nowak, D., De La Maza, C.L., Rodríguez, M., Crane, D., 2008. Analyzing the cost effectiveness of Santiago, Chile's policy of using urban forests to improve air quality. Journal of Environmental Management 86, 148–157.

Fall, R., 1999. Biogenic emissions of volatile organic compounds from higher plants. In: Hewitt, C.N. (Ed.), Reactive Hydrocarbons in the Atmosphere. Academic Press, New York.

Faoro, F., Iriti, M., 2009. Plant cell death and cellular alterations induced by ozone: key studies in Mediterranean conditions. Environmental Pollution 157, 1470–1477.

Fowler, D., Pilegaard, K., Sutton, M.A., Ambus, P., Raivonen, M., Duyzer, J., Simpson, D., Fagerli, H., Fuzzi, S., Schjoerring, J.K., Granier, C., Neftel, A., Isaksen, I., Laj, P., Maione, M., Monks, P.S., Burkhardt, J., Daemmgen, U., Neirynck, J., Personne, E., Wichink-Kruit, R., Butterbach-Bahl, K., Flechard, C., Tuovinen, J.P., Coyle, M., Gerosa, G., Loubet, B., Altimir, N., Gruenhage, L.,

Ammann, C., Cieslik, S., Paoletti, E., Mikkelsen, T.N., Ro-Poulsen, H., Cellier, P., Cape, J.N., Horvath, L., Loreto, F., Niinemets, Ü., Palmer, P.I., Rinne, J., Misztal, P., Nemitz, E., Nilsson, D., Pryor, S., Gallagher, M.W., Vesala, T., Skiba, U., Brüggemann, N., Zechmeister-Boltenstern, S., Williams, J., Dowd, C., Facchini, M.C., De Leeuw, G., Flossman, A., Chaumerliac, N., Erisman, J.W., 2009. Atmospheric composition change: ecosystems – atmosphere interactions. Atmospheric Environment 43, 5193–5267.

Geron, C., Harley, P., Guenther, A., 2001. Isoprene emission capacity for US tree species. Atmospheric Environment 35, 3341–3352.

Guenther, A.B., Zimmerman, P.R., Harley, P.C., 1993. Isoprene and monoterpene variability: model evaluations and sensitivity analysis. Journal of Geophysical Research 98, 12609–12617.

Guenther, A., Zimmerman, P., Wildermuth, M., 1994. Natural volatile organic compound emission rate estimates for U.S. woodland landscapes. Atmospheric Environment 28 (6), 1197–1210.

Guenther, A., Hewitt, C.N., Erickson, D., Fall, R., Geron, C., Graedel, T., Harley, P., Klinger, L., Lerdau, M., Mckay, W.A., Pierce, T., Scholes, B., Steinbrecher, R., Tallamraju, R., Taylor, J.Y., Zimmerman, P., 1995. A global model of natural volatile organic compound emissions. Journal of Geophysical Research 100 (5), 8873–8892.

Guenther, A., Zimmermann, P., Klinger, L., Greenberg, J., Ennis, C., Davis, K., Pollock, W., 1996. Estimates of regional natural volatile organic compound fluxes from enclosure and ambient measurements. Journal of Geophysical Research 101, 1345–1359.

Günthardt-Georg, M.S., Vollenweider, P., 2007. Linking stress with macroscopic and microscopic leaf response in trees: new diagnostic perspectives. Environmental Pollution 147, 467–488.

Hakola, H., Rinne, J., Laurila, T., 1998. The hydrocarbon emission rates of tea-leafed willow (*Salix phylicifolia*), silver birch (*Betula pendula*) and European aspen (*Populus tremula*). Atmospheric Environment 32 (10), 1825–1833.

Health-Canada and Environment-Canada, 1999. National Ambient Air Quality Objectives for Ground-level Ozone.

Hernández, J., Benjumeda, A., Fernández, L., Prieto, R., Chaparro, A., De La Calle, A., 2002. Oleáceas. In: Valero Santiago, A.L., Cadahía García, Á. (Eds.), Polinosis. MRA Ediciones, S.L. España, pp. 99–119. Capítulo 4.1.

IPCC, 2007. Climate change. The physical science basis. In: Solomon, S., Qin, D., Manning, M., Marquis, M., Tignor, M.M.B., Miller Jr., H.L., Chen, Z. (Eds.), Working group I. Contribution to the Fourth Assessment Report of the Intergovernmental Panel on Climate Change. Cambridge University Press, pp. 1–996.

IUPAC. http://www.chem.qmul.ac.uk/iupac/class/terp.html (consultation: 01.10.12.).

Kansal, A., 2009. Sources and reactivity of NMHCs and VOCs in the atmosphere: a review. Journal of Hazardous Materials 166, 17–26.

Kegge, W., Pierik, R., 2010. Biogenic volatile organic compounds and plant competition. Trends in Plant Science 15 (3), 126–132.

Kesselmeier, J., Staudt, M., 1999. Biogenic Volatile Organic Compounds (VOC): an overview on emission, physiology and ecology. Journal of Atmospheric Chemistry 33, 23–88.

Kesselmeier, J., Schäfer, L., Ciccioli, P., Brancaleoni, E., Cecinato, A., Frattoni, M., Foster, P., Jacob, V., Denis, J., Fugit, J.L., Dutaur, L., Torres, L., 1996. Emission of monoterpenes and isoprene from a Mediterranean oak species *Quercus ilex* L. measured within the BEMA (Biogenic Emissions in the Mediterranean Area) project. Atmospheric Environment 30, 1841–1850.

König, G., Brunda, M., Puxbaum, H., Hewitt, C.N., Duckham, S.C., Rudolph, J., 1995. Relative contribution of oxygenated hydrocarbons to the total biogenic VOC emissions of selected mid-European agricultural and natural plant species. Atmospheric Environment 29, 861–874.

Kroll, J., Ng, N., Murphy, S., Flagan, R., Seinfeld, J., 2006. Secondary organic aerosol formation from isoprene photooxidation. Environmental Science and Technology 40 (6), 1869–1877.

Lamb, B., Westberg, H., Quarles, T., Flyckt, D., 1983. Natural Hydrocarbon Emission Rate Measurements from Vegetation in Pennsylvania and Washington. Report PB84-124981. U.S. Environmental Protection Agency, Nat. Tech. Inf. Serv, Springfield, Virginia, U.S.A.

Lelieveld, J., Butler, T.M., Crowley, J., Dillon, T., Fischer, H., Ganzeveld, L., Harder, H., Lawrence, M.G., Martinez, M., Taraborrelli, D., 2008. Atmospheric oxidation capacity sustained by a tropical forest. Nature 452, 737–740.

Liakakoua, E., Vrekoussisa, M., Bonsangb, B., Donousisa, Ch., Kanakidoua, M., Mihalopoulos, N., 2007. Isoprene above the Eastern Mediterranean: seasonal variation and contribution to the oxidation capacity of the atmosphere. Atmospheric Environment 41, 1002–1010.

Loreto, F., Schnitzler, P., 2010. Abiotic stresses and induced BVOCs. Trends in Plant Science 15 (3), 154–166.

Mauzerall, D., Wang, X., 2001. Protecting agricultural crops from the effects of tropospheric ozone exposure: reconciling Science and Standard Setting in the United States, Europe, and Asia. Annual Review Energy Environment 26, 237–268.

Mills, G., Pleijel, H., Braun, S., Büker, P., Bermejo, V., Calvo, E., Danielsson, H., Emberson, L., González, I., Grünhage, L., Harmens, H., Hayes, F., Karlsson, P., Simpson, D., 2011. New stomatal flux-based critical levels for ozone effects on vegetation. Atmospheric Environment 45, 5064–5068.

MMA (Ministerio del Medioambiente, Chile). http://www.seremisaludrm.cl/sitio/pag/aire/indexjs3aireglosario.asp#ozono (consultation 05.03.12.).

Morales, R., 2006. In: Morales, R. (Ed.), Contaminación Atmosférica Urbana. Episodios críticos de contaminación ambiental en la ciudad de Santiago. Editorial Universitaria, Santiago de Chile.

Motta, A.C., Marliere, M., Peltre, G., Sterenberg, P.A., Lacroix, G., 2006. Traffic-related air pollutants induce the release of allergen-containing cytoplasmic granules from grass pollen. International Archives of Allergy and Immunology 139, 294–298.

Moukhtar, S., Couret, C., Rouil, L., Simon, V., 2006. Biogenic Volatile Organic Compounds (BVOCs) emissions from *Abies alba* in a French forest. Science of the Total Environment 354, 232–245.

Nagegowda, D.A., 2010. Plant volatile terpenoid metabolism: biosynthetic genes, transcriptional regulation and subcellular compartmentation. FEBS Letters 584, 2965–2973.

Niinemets, Ü., Loreto, F., Reichstein, M., 2004. Physiological and physicochemical controls on foliar volatile organic compound emissions. Trends in Plant Science 9, 180–186.

Nowak, D., Kevin, L., Rao, S., Sistia, G., Luley, C., Crane, D., 2000. A modeling study of the impact of urban trees on ozone. Atmospheric Environment 34, 1601–1603.

Owen, S., Harley, P., Guenther, A., Hewitt, C., 2002. Light dependency of VOC emissions from selected Mediterranean plant species. Atmospheric Environment 36, 3147–3159.

Pacífico, F., Harrison, S., Jones, C., Sitch, S., 2009. Isoprene emissions and climate. Atmospheric Environment 43, 6121–6135.

Padhy, P., Varshney, C., 2005. Isoprene emission from tropical tree species. Environmental Pollution 135, 101–109.

Paoletti, E., Manning, W.J., 2007. Toward a biologically significant and usable standard for ozone that will also protect plants. A Review. Environmental Pollution 150, 85–95.

Papiez, M., Potosnak, M., Goliff, W., Guenther, A., Matsunaga, S., Stockwell, W., 2009. The impacts of reactive terpene emissions from plants on air quality in Las Vegas, Nevada. Atmospheric Environment 43, 4109–4123.

Park, Hun Myoung, 2009. Comparing Group Means: T-tests and One-way ANOVA Using STATA, SAS, R, and SPSS. Working Paper. The University Information Technology Services (UITS) Center for Statistical and Mathematical Computing, Indiana University. Available on line: http://www.indiana.edu/~statmath/stat/all/ttest.

Peñuelas, J., Staudt, M., 2010. BVOCs and global change. Trends in Plant Science 15 (3), 133–144.

Pinto, D., Blande, J., Nykänen, R., Dong, W., Nerg, M., Holopainen, J., 2007. Ozone degrades common herbivore-induced plant volatiles: does this affect herbivore prey location by predators and parasitoids? Journal of Chemical Ecology 33, 683–694.

Préndez, M., Peralta, H., 2005. Determinación de Factores de Emisión de Compuestos Orgánicos Volátiles de dos Especies Arbóreas Nativas de La Región Metropolitana, Chile. Información Tecnológica 16 (1), 17–27 (in spanish).

Préndez, M., Alvarado, G., Serey, I., 2011. Some guidelines to improve air quality management in Santiago, Chile: from commune to basin level. In: Mazzeo, N. (Ed.), Air Quality Monitoring, Assessment and Management. INTECH Open Access Publisher, pp. 305–328.

Quinn, G., Keough, M., 2002. Experimental Design and Data Analysis for Biologist. Cambridge University Press.

R Core Team, 2013. A Language and Environment for Statistical Computing. R Foundation for Statistical Computing, Vienna, Austria. Available on line: http://www.R-project.org.

Rappenglück, B., Oyola, P., Olaeta, I., Fabian, P., 2000. The evolution of photochemical smog in the Metropolitan Area of Santiago de Chile. Journal of Applied Meteorology 39, 275–290.

Roukos, J., Riffault, V., Locoge, N., Plaisance, H., 2009. VOC in an urban and industrial harbor on the French North Sea coast during two contrasted meteorological situations. Environmental Pollution 157, 3001–3009.

Screpanti, A., De Marco, A., 2009. Corrosion on cultural heritage buildings in Italy: a role for ozone? Environmental Pollution 157, 1513–1520.

Seguel, R.J., Morales, R.G., Leiva, M.A., 2012. Ozone weekend effect in Santiago, Chile. Environmental Pollution 162, 72–79.

Sharkey, T., Yeh, S., 2001. Isoprene emission from plants. Plant Physiology and Plant Molecular Biology 52, 407–436.

Sillman, S., 1999. The relation between ozone, NO_x and hydrocarbons in urban and polluted rural environments. Atmospheric Environment 33, 1821–1845.

Simon, V., Dumergue, L., Solignac, G., Torres, L., 2005. Biogenic emissions from *Pinus halepensis*: a typical species of the Mediterranean area. Atmospheric Research 74, 37–48.

Tsui, J.K., Guenther, A., Yip, W.K., Chen, F., 2009. A biogenic volatile organic compound emission inventory for Hong Kong. Atmospheric Environment 43, 6442–6448.

Viñas, M., 2002. Betuáceas. Capítulo 4.2. In: Valero Santiago, A.L., Cadahía García, Álvaro (Eds.), Polinosis. MRA Ediciones, S.L. España, pp. 121–128.

WHO, 2000. World Health Organization, Air Quality Guidelines for Europe. In: European Series, N° 91. Regional Office for Europe, Copenhagen.

WHO, 2011. World Health Organization Media Centre, Air Quality and Health, Fact Sheet N°313. Updated September 2011 [in line]. http://www.who.int/mediacentre/factsheets/fs313/es/index.html (consultation: 23.11.11.).

Winer, A.M., Fitz, D.R., Miller, P.R., 1983. Investigation of the Role of Natural Hydrocarbons in Photochemical Smog Formation in California. Contract No. AO-056-32, prepared for the California Air Resources Board, by the Statewide Air Pollution Research Center, Riverside, California, U.S.A..

Winer, A., Arey, J., Atkinson, R., Aschmann, S., Long, W., Morrisom, L., Olszyk, D., 1992. Emission rates of organics from vegetation in California's central valley. Atmospheric Environment 26a, 2647–2659.

Zar, J., 1999. Biostatistical Analysis, fourth ed. Prentice Hall, Englewood Cliffs, New Jersey.