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1 Interannual Variability of BVOC Emissions in an Alpine City

2 Lisa Kaser[1], Arianna Peron[1], Martin Graus[1], Marcus Striednig[1], Georg Wohlfahrt[2] , Stanislav
3 Juráň[3], Thomas Karl[1]

4 [1]Department of Atmospheric and Cryospheric Sciences, University of Innsbruck, Innrain 52f, 6020
5 Innsbruck, Austria
6 [2]Department of Ecology, University of Innsbruck, Sternwartestrasse. 15, 6020 Innsbruck, Austria
7 [3] Global Change Research Institute of the Czech Academy of Sciences, Bělidla 986/4a, 603 00 Brno,
8 Czech Republic

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10 *Correspondence to*: Thomas Karl (thomas.karl@uibk.ac.at) and Lisa Kaser (kaser.lisa@gmail.com)

11 **Abstract.** Terpenoid emissions above urban areas are a complex mix of biogenic and anthropogenic
12 emission sources. In line with previous studies we found that summertime terpenoid emissions in an
13 alpine city were dominated by biogenic sources, but especially at lower temperatures the anthropogenic
14 influences were non-negligible. Inter-seasonal emission measurements revealed consistency for
15 monoterpenes and sesquiterpenes, but a large difference in isoprene between the summers 2015 and
16 2018. Standardized emission potentials for monoterpenes and sesquiterpenes were 0.12 nmol m^{-2} s^{-1} and
17 $3.0 \cdot 10^{-3}$ nmol m^{-2} s^{-1} in 2015 and 0.11 nmol m^{-2} s^{-1} and $3.4 \cdot 10^{-3}$ nmol m^{-2} s^{-1} in 2018, respectively.
18 Observed isoprene emissions were about four times higher in 2018 than in 2015. This factor decreased
19 to 2.3 after standardizing isoprene emissions to 30°C air temperature and photosynthetic active radiation
20 (PAR) of 1000 μmol m^{-2} s^{-1}. Based on emission model parameterizations, increased leaf temperatures
21 can explained ~50% of these differences, but standard emission potentials remained higher in 2018,
22 when a heat wave persisted. Potential other reasons for the differences such as emission
23 parameterization, footprint changes, water stress conditions and tree trimming are investigated.

1 Introduction

25 Biogenic and anthropogenic volatile organic compounds (BVOCs, AVOCs) in the atmosphere can
26 contribute to surface air pollution both due to their influence on tropospheric ozone formation and due
27 to their potential to act as precursors for secondary organic aerosol formation (Derwent et al., 1996,
28 Fehsenfeld et al., 1992, Fuentes et al., 2000, Goldstein et al., 2009, Laothawornkitkul et al., 2009,
29 Riipinen et al., 2012). BVOCs are playing a particularly important role globally, as their emission
30 strength is estimated to be 10 times larger than AVOCs (Guenther et al., 2012, Piccot et al., 1992). Also,
31 many BVOCs are characterized as highly reactive (Atkinson and Arey, 2003, Fuentes et al., 2000),
32 resulting in rapid peroxy radical chemistry important for ozone and ultra-fine particle formation

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33   processes (Simon et al., 2020). Of the total global BVOC emissions, terpenes dominate, with 50%
34   attributed to isoprene, 15% to monoterpenes and about 0.5% to sesquiterpenes (Guenther et al., 2012).
35   In forests with predominating isoprene emissions, isoprene was found responsible for 50-100% of the
36   tropospheric ozone production (Duene et al., 2002, Tsigaridis and Kanakidou, 2002, Poisson et al.,
37   2001). In coniferous forests monoterpene and sesquiterpene emissions often dominate (Johansson and
38   Janson, 1993, Thunis and Cuvelier, 2000, Juráň et al., 2017). It has been shown that RO_2 self-reactions
39   of monoterpenes and sesquiterpenes can rapidly create highly oxidized matter (HOM) and are a key
40   player for new particle formation (NPF) events in forests under low NOx conditions (Simon et al.,
41   2020).
42   In urban environments where the mixture of BVOCs and AVOCs is more complex, several recent
43   studies point out the importance of biogenic emissions for local air quality (Simon et al., 2019, Bonn et
44   al., 2018, Churkina et al., 2017, Ren et al., 2017, Papiez et al., 2009, Chameides et al., 1988) and that
45   the BVOC influence is especially high during summertime heat waves (Churkina et al. 2017).
46   Particularly in summer, biogenic sources are dominating in urban environments. E.g., Yadav et al.
47   (2019) found an increased importance of biogenic isoprene in an urban site in western India during pre-
48   monsoon season when temperatures and PAR were high, Hellen et al. (2012) found a strong biogenic
49   influence on isoprene and monoterpene concentrations in Helsinki in July. Summertime isoprene in two
50   large Greek cities was appointed with PMF to come 60-70% from vegetation (Kaltsonoudis et al. 2016).
51   Yang et al. (2005) showed a strong seasonal and daily cycle in isoprene contributing it therefore to
52   biogenic sources in an urban region in Taiwan. Borbon et al (2002) showed that biogenic sources
53   strongly superimpose the traffic emissions of isoprene in summer in an urban area in France. Wagner
54   and Kuttler (2014) found that during summer afternoons in an urban area in Germany anthropogenic
55   influences on isoprene concentrations were negligible. Chang et al. (2014) and Wang et al. (2013)
56   showed that in a tropical-subtropical metropolis biogenic contributions overwhelmed anthropogenic
57   contributions of isoprene in summer and that biogenic sources started to dominate in all seasons above a
58   threshold temperature of 17-21°C. Whereas all so far cited studies were based on concentration
59   measurements where the influence can be both local and regional and strongly modulated by
60   atmospheric dilution the following studies were based on eddy covariance flux tower sites: At
61   temperatures over 25°C more than 50% of the isoprene flux was found to be biogenic in origin in
62   London with a mean daytime flux of 0.18 mg m^{-2} h^{-1} (Langford et al. 2010). Similarly, Valach et al.
63   (2015) in a different study in London found a mean daytime flux of 0.2 mg m^{-2} h^{-1}. Kota et al. (2014)
64   found a daytime median flux of 2.1 mg m^{-2} h^{-1} over Houston, Texas and contributed it to mostly
65   biogenic sources. Park et al (2010) found also in Houston, Texas a daytime isoprene flux of 0.7 mg m^{-2}
66   h^{-1}. Rantala et al. (2016) found that 80% of the measured 10 ng m^{-2} s^{-1} summer daytime isoprene flux
67   near Helsinki could be contributed to biogenic sources by comparing emissions at low and high
68   temperatures.
69   While there is evidence for urban trees to have positive influence on urban environments such as
70   mitigating the urban heat island effect, sequestering CO_2 and particles as well as acting as storm water
71   interception (Escobedo et al., 2011, Connop et al., 2016, Livesley et al., 2016), BVOC emissions of
72   urban trees and their subsequent effect on air pollution is very plant species dependent (Corchnoy et al.,
73   1992, Steinbrecher et al., 2009, Fitzky et al., 2019) and should be taken into account when planting
74   urban trees (Calfapietra et al., 2013, Churkina et al., 2015, Ren et al., 2017). Emerging evidence that

75 isoprene derived RO_2 competes with RO_2 radicals from higher molecular weight terpenes in the
76 formation of new particles highlights the need to study emissions in different environments (Berndt et
77 al. 2018).
78 To assess the status quo of BVOC emissions in a city or area and their impact on local air quality urban
79 eddy covariance flux measurements have become available for some urban areas (Langford et al. 2010,
80 Park et al 2010, Kota et al. 2014, Valach et al. 2015, Rantala et al. 2016).
81 Few studies characterize the seasonal and interannual changes of BVOCs and even fewer studies are
82 available in urban environments: Chang et al. (2014) measured seasonal changes in urban isoprene
83 concentrations in Taipei revealing the biogenic dominance of isoprene in daytime concentrations of
84 biogenic sources for spring, summer and fall and even a dominance of biogenic sources at night in
85 summer. Valach et al. (2015) showed decreasing isoprene fluxes transitioning from summer to winter at
86 a central London measurement site. Vaughan et al. (2017) report airborne flux measurements over
87 South Sussex of two consecutive summers showing different isoprene emissions that can be explained
88 by different temperature and cloud cover conditions. Warneke et al. (2010) tried to explain the
89 measured interannual differences of a factor of 2 in emissions of isoprene and monoterpene over Texas
90 by temperature, drought effects or influences from changes in leaf area index (LAI). Palmer et al.
91 (2006) found a maximum of 20-30% interannual difference in isoprene emissions using satellite-based
92 isoprene quantification from formaldehyde measurements over North America. A model study by
93 Steinbrecher et al. (2009) found only a 10% annual difference in biogenic emissions from cold to hot
94 years. Gulden et al. (2007) found that, on a regional scale, variations in leaf biomass density driven by
95 variations in precipitation are together with temperature and shortwave radiation variations the most
96 important factors for variations in BVOC emissions. Tawfik et al. (2012) found in a model study that
97 interannual variation of isoprene emission is with 18% strongest in July with temperature and soil
98 moisture explaining 80% of the variations, whereas the influences of variations in photosynthetic active
99 radiation (PAR) and LAI were negligible. In a three-year study over a northern hardwood forest,
100 Pressley et al. (2005) found that total cumulative isoprene emissions varied only by 10%.
101 Given the current lack of multi-year urban VOC flux measurements and our limited understanding of
102 the interannual variability of biogenic and anthropogenic emission sources, the objective of the present
103 study was to quantify the interannual variation of the urban ecosystem-atmosphere exchange of the
104 three major isoprenoids, isoprene, monoterpenes and sesquiterpenes, and to analyze the underlying
105 drivers. We hypothesized (i) that the exchange of these BVOCs can be attributed largely to the spatio-
106 temporal variability of biogenic sources and (ii) that differences in environmental forcings are the main
107 drivers of interannual variability. To address these hypotheses, urban eddy covariance BVOC flux
108 measurements during two growing seasons above the city of Innsbruck (Austria) are blended with
109 bottom-up emission estimates based on a process-based model and a detailed urban tree inventory.

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2 Materials and methods

2.1 Field site and instruments

VOC concentrations and flux measurements were conducted during two comparable summer periods (July10-September 9 2015 & July 27-September 2 2018) close to the city center of Innsbruck on the rooftop of one of the tallest buildings in the area. Details on the Innsbruck Atmospheric Observatory (IAO) measurement site and instrument performance were published by Karl et al. (2018) and Striednig et al. (2020). Therefore, we give here only a short summary of the study location and measurement details. The measurement location ($47°15'51.66''$ N, $11°23'06.82''$ E) is shown in Figure 1A on a 1000x1000m map surrounding the site. This will in the following be referred to as the study area. The dominant wind direction at the IAO is NE during the daytime and SW during nighttime (Karl et al. 2020, Striednig et al. 2020).

3D sonic wind, CO_2, and H_2O were measured with a CPEC200 (Campbell Scientific) eddy covariance system on a tower on top of the building 42 m above street level. A heated inlet line led from the tower to a close-by laboratory hosting a PTR-QiTOF-MS instrument (IONICON Analytik, Sulzer et al. 2014). Both summers the PTR-QiTOF-MS was operated in H_3O^+ mode with standard drift tube conditions of 112 Townsend (E/N electric field strength). Regular instrument calibrations and zeroing revealed typical acetone and isoprene sensitivities of 1550 and 950 Hz/ppbv respectively. 3D wind and VOCs were sampled at 10 Hz.

Incident PAR was calculated from short wave radiation measured by a pyranometer (Schenk 8101, Schenk, Wien) applying the relationship derived by Jacovides et al. (2003).

Precipitation data were collected 400 m south of our field site by a MPS TRWS 503 tipping bucket precipitation gauge and a Thies 5.4103.10.000 precipitation monitor, mounted at 1.5 m above a grass surface.

Plant available soil moisture for 2015-2019 was retrieved as the SMAP level 4 3-hourly 9 km rootzone soil moisture product (Reichle et al. 2018) via the AppEEARS interface (https://lpdaacsvc.cr.usgs.gov/appeears/).

2.2 Eddy covariance fluxes

This study focuses on biogenic emissions collected during summer 2015 and summer 2018. As biogenic emissions are strongly light- and temperature-driven, the total available dataset was reduced to daytime hours (9:00-16:00 local time) and mean wind directions from 0°-120°. Data with wind direction from the south and exceeding a wind speed > 10 m/s were excluded as they can be attributed to foehn events. Eddy covariance fluxes were calculated using a MATLAB® code described by Striednig et al. (2020). As a QA/QC criteria for fluxes we implemented a combination of steady state filter of the respective scalar, the integral turbulence characteristics test of the wind components and flow sector filtering, similar to the combination described in Chapter 4.2.5. in Foken (2017) with a required overall quality class of 6 or lower. According to Foken (2017), classes 1-6 can be used for long-term measurements of fluxes without limitations.

Footprint and footprint density were calculated following Kljun et al. (2015).

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148   We standardized isoprene eddy covariance fluxes $E_{0,ISO}$, to a temperature of 303.15 K and PAR of 1000
149   µmol m^{-2} s^{-1} using a model described in detail by Guenther et al. (2006): $E_{ISO} = E_{0,ISO} * \gamma_T * \gamma_P$, where
150   γ_T and γ_P are temperature- and light-dependent coefficients respectively containing current and past
151   (24h and 240h) conditions. In order to investigate relative inter-seasonal changes of isoprene emissions
152   the MEGAN 5-layer canopy model (Guenther et al., 2006) was applied.
153   Monoterpene and sesquiterpene eddy covariance fluxes are known to be purely temperature dependent
154   and can be described as:$E_{MT} = E_{0,MT} * C_{T,MT}$ and $E_{SQT} = E_{0,SQT} * C_{T,SQT}$ where C_T is a temperature
155   dependent factor described by Guenther et al. (1994).
156   In the case of sesquiterpenes, turbulent time scales (100 s) are on the order of chemical time scales as
157   sesquiterpenes can react fast with ozone (typical ozone concentrations were 30 ppbv). The chemical loss
158   was estimated by the following equation: c(t)/c0=exp(-t_{turb}/t_{chem}) where t_{turb} is the turbulent time scale
159   and t_{chem} the chemical time scale.

2.3 City tree inventory

161   An inventory of all trees planted by the city municipality is available for the city of Innsbruck, Austria
162   containing location, tree species, diameter at breast height and height. However, this inventory does not
163   include trees from private gardens. Therefore, all accessible trees from private gardens were identified
164   and added to the existing tree inventory. The location of the trees from the city inventory and private
165   gardens in the study area are shown in Figure 1A. Within the study area a total of 1904 registered trees
166   distributed across 129 tree species were counted. A list of the 44 most abundant tree species, where the
167   species count in the study area was 6 or more, is given in Table 1.

2.4 Emission potentials

169   Literature values of plant-species specific emission potentials of isoprene and monoterpene, in µg
170   compound g^{-1} dry-weight h^{-1} standardized to 303.15 K and PAR 1000 µmol m^{-2} s^{-1} were assigned to the
171   44 most abundant species in the study area. This includes all tree species with an occurrence larger than
172   6 individuals within the footprint and accounts for ~90% of the total counted trees. Emission potential
173   assignment was based on the detailed work by Stewart et al. (2003) for the overlapping species. Other
174   emission potentials were taken from other literature and if more than one literature value was available,
175   an average was taken. All species, emission potentials and references thereof are shown in Table 1.
176   Sesquiterpene (SQT) emission potentials were taken from Karl et al. (2009) and if not reported therein
177   the average value of 0.1 µg compound g^{-1} dry-weight h^{-1} was assigned.

2.5 Relative IS, MT, SQT emission ratio maps

179   To generate emission ratio maps, the study area was divided into a 100 m by 100 m grid and tree
180   species were counted in each grid tile and multiplied by their emission potential listed in Table 1. The
181   resulting map in units of µg compound g^{-1} dry-weight h^{-1} neglects the actual, but unknown, amount of
182   dry leaf weight of each individual tree.

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183   Due to the unknown amount of emitting leaf material, it is difficult to compare bottom-up estimates
184   from this method with direct eddy covariance flux measurements. A more robust comparison is possible
185   when relative emission maps are investigated such as ISO/MT, ISO/SQT and SQT/MT. For this we first
186   added up all individual tree emission factors in each tile (e.g. $ISO_{square} = \sum ISO_{tree}$) and then divided
187   these by the tile emission factors e.g. ISO_{tile}/MT_{tile}. For simplicity this is in the following called
188   ISO/MT. ISO/MT is then multiplied with the footprint density in each tile and summed up over the total
189   study area. This is a bottom-up ISO/MT ratio expected at the measurement site.

190   **3 Results and discussion**

191   **3.1 Flux footprint, light & temperature conditions**

192   The flux footprint of the daytime data at the IAO is shown in Figure 1A plotted on a map of 1000 m x
193   1000 m surrounding the flux tower location. 60% of the flux footprint density lay, in both years, entirely
194   within the study area. The footprint area extended slightly farther in 2015 than in 2018. The relative
195   contribution of the land cover types in both years however was similar with 40-41% buildings, 23%
196   paved areas, 25-28% roads, 5% trees, 5% short vegetation, and <1% water. Within the 60% flux
197   footprint area in 2015 and 2018 lay 148 and 89 individual trees of the tree inventory distributed over 33
198   and 24 tree species, respectively. Combining the tree inventory with literature values on basal emission
199   factors (Table 1) and the footprint density calculated for each tree location revealed that 60% and 70%
200   of the bottom-up isoprene emissions arriving at the flux tower were from 12 trees in 2015 and 2018
201   respectively. These were trees closest to the footprint density maximum and trees with high isoprene
202   basal emission factors. The tree species were *Populus nigra*, *Platanus acerifolia, Sophora japonica*, and
203   *Quercus robur.* As the footprint area was smaller in 2018 compared to 2015, the relative importance of
204   the emission of these trees was higher in 2018 than in 2015. Bottom-up monoterpene emissions were
205   distributed more evenly among different tree species: 19 trees in the study area accounted for ~50% of
206   the bottom-up MT emissions arriving at the flux tower. The most important species were *Aesculus*
207   *carnea*, *Pinus sylvestris*, *Larix decidua,* and *Acer platanoides*. Sesquiterpene bottom-up emissions were
208   even more equally distributed over the tree species: 38 trees accounted for 50% and 60% of bottom-up
209   SQT emissions arriving at the flux tower in 2015 and 2018 respectively. *Betula pendula* and *Sophora*
210   *japonica* contributed 20% and 12% to the emissions arriving at the tower in 2015 and 22% and 19% in
211   2018. Diurnal cycles of PAR and air temperature, two of the strongest biogenic emission drivers, are
212   shown in Figure 1B and 1C, respectively. While PAR was very similar during the two summers, mean
213   air temperatures in 2018 were 2K higher during daytime and 1.5K higher during nighttime compared to
214   2015. The higher temperatures in 2018 coincided with an intense heat wave. Monthly average
215   temperatures in August 2018 were 3K above the climatological mean values (1981-2010).
216
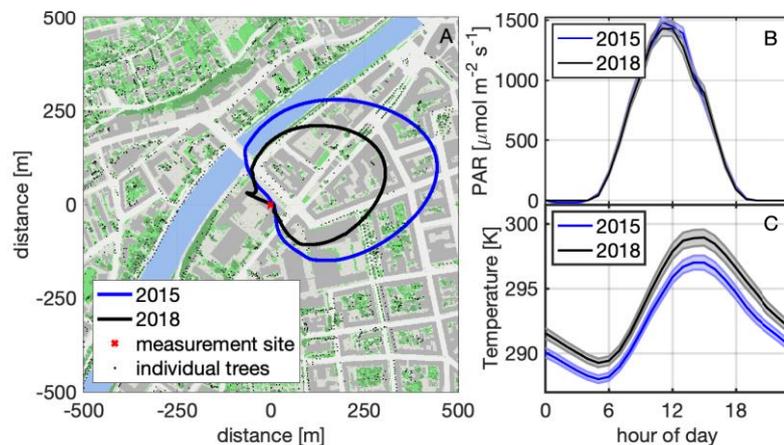
Figure 1: A) Map surrounding the Innsbruck Atmospheric Observatory (indicated with a red cross in the center) depicting trees, short vegetation, water, roads, paved areas and buildings in dark green, light green, blue, white, light grey and dark grey respectively. Black dots represent individual trees from the city tree inventory. The 60% daytime (9:00-16:00) footprint areas with mean wind directions between 0° and 120° are shown in blue and black for summer 2015 and 2018 respectively. B) Diurnal cycle of average and standard error of PAR. C) Diurnal cycle of average and standard error of ambient temperature 2015 (blue) and 2018 (black) Maps were created in Matlab (www.mathworks.com) and are based on OpenStreetMap (https://www.openstreetmap.org/copyright) under the CC BY 3.0 AT license.

3.2 Two summers of urban BVOC fluxes

Biogenic isoprene emissions are light and temperature dependent (e.g. Guenther et al. 1993), while biogenic monoterpene and sesquiterpene emissions are mostly temperature dependent (e.g. Guenter et al. 1994). Karl et al. (2018) showed that isoprene and monoterpene at this measurement site are linked to biogenic processes. Figure 2 A-C shows the average diurnal cycles of isoprene, monoterpene and sesquiterpene fluxes. Daytime maxima of isoprene emissions were 0.4 nmol m^{-2} s^{-1} and 1.2 nmol m^{-2} s^{-1} in 2015 and 2018 respectively. Estimates based on winter-time benzene/isoprene flux ratios reveal that an upper limit of 20-30% of the daytime isoprene flux was anthropogenic in origin and the larger isoprene source at this site was biogenic. This is in good accordance with previous studies conducted in urban environments (Kota et al. 2014, Park et al 2010, Rantala et al. 2016). The large interannual difference and its potential reasons are discussed further in section 3.3.
Maximum average daytime monoterpene fluxes were 0.13 nmol m^{-2} s^{-1} and 0.18 nmol m^{-2} s^{-1} for 2015 and 2018, respectively, and average daytime sesquiterpene fluxes were 5·10^{-3} nmol m^{-2} s^{-1} in both years. All data binned into 2K temperature ranges of all three species and both summers are shown in Figure 2 D-F. Fig. 2D shows a good match with the theoretical temperature curve from Guenther et al. (1993) for isoprene emissions of both summers. The interannual difference, discussed further in section 3.3, persisted at higher temperatures. Measured monoterpene and sesquiterpene measured fluxes at lower temperatures (280K-295K) were higher than the predicted values based on the Guenther et al. (1994) algorithm. This could be an indication that at lower temperatures other, non-biogenic sources contributed to monoterpene and sesquiterpene fluxes at this site. At temperatures higher than 295K, MT and SQT fluxes followed known temperature dependencies.

247 Standardizing the fluxes removes the variability due to current temperature and light conditions and
248 allows for interannual comparison as well as comparison to other studies. Standardized isoprene fluxes
249 (standardized to 303.15K and PAR 1000 μ mol m^{-2} s^{-1} not including 24h and 240h temperature and
250 light history) were 0.58±0.01 nmol m^{-2} s^{-1} and 1.33±0.06 nmol m^{-2} s^{-1} in 2015 and 2018 respectively.
251 Isoprene fluxes from both years were lower than what Rantala et al. (2016) found for an urban flux site
252 in Helsinki, where the standardized emission potential was 125 ng m^{-2} s^{-1} (eq. to: 1.8 nmol m^{-2} s^{-1}). The
253 Helsinki flux site had a larger vegetation cover of 38-59% compared to our study area, where the
254 vegetation cover was estimated to be 10% within the flux footprint. Park et al. (2010) reported a
255 standard emission rate of isoprene of 0.53 mg m^{-2} h^{-1} (eq. to: 2.2 nmol m^{-2} s^{-1}) over Houston, Texas,
256 which is higher than both our 2018 and 2015 measurements. This is potentially due to a higher
257 vegetation cover in Houston as well as strong isoprene-emitting oaks within the footprint of the
258 measurement site. Valach et al. (2015) reported a daytime average flux in August of 0.3 mg m^{-2} h^{-1} (eq.
259 to: 1.2 nmol m^{-2} s^{-1}) at an urban site in London and Acton et al. (2020) a summer daytime average
260 isoprene flux of 4.6 nmol m^{-2} s^{-1} at an urban site in Beijing, both however cannot be directly compared
261 to our measurements as their values were not standardized to temperature and PAR.
262 Average daytime standardized monoterpene fluxes were, with 0.12 and 0.11 nmol m^{-2} s^{-1} in 2015 and
263 2018, respectively, relatively similar between the two summers. Average daytime standardized
264 sesquiterpene fluxes were over a magnitude smaller than standardized monoterpene fluxes and were
265 comparable between the two summers with mid-day values on the order of $3.0 \cdot 10^{-3}$ nmol m^{-2} s^{-1} and
266 $3.5 \cdot 10^{-3}$ nmol m^{-2} s^{-1} in 2015 and 2018 respectively. As the turbulent time scale and the chemical
267 lifetime of sesquiterpenes with respect to destruction by ozone were similar, we calculated an upper
268 limit of the correction factor of 2.5. This means that, when correcting for reactive losses of
269 sesquiterpenes with ozone, sesquiterpene emissions could have been up to 2.5 times higher than the
270 measured values leading to an upper limit of daytime standardized sesquiterpene emission of $7.5 \cdot 10^{-3}$
271 nmol m^{-2} s^{-1} and $8.8 \cdot 10^{-3}$ nmol m^{-2} s^{-1} in 2015 and 2018, respectively.
272

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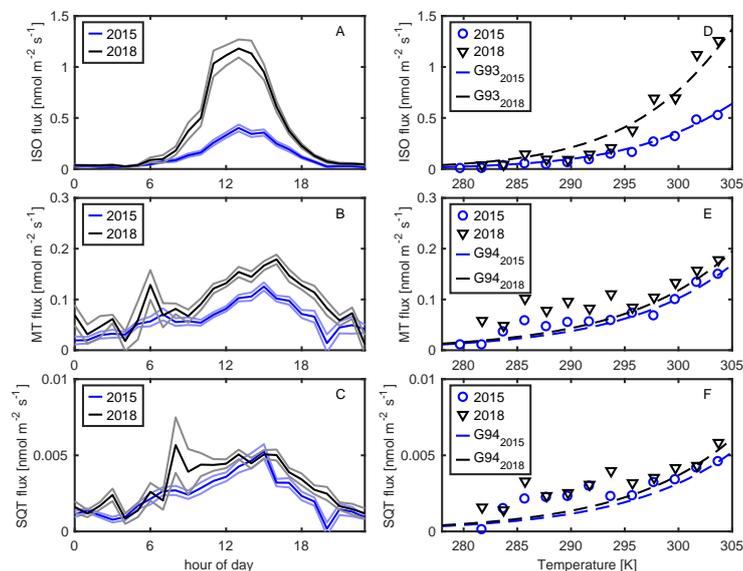
274
275 **Figure 2: Diurnal cycles of average isoprene (A), monoterpene (B) and sesquiterpene (C) fluxes for the summers 2015 (blue) &**
276 **2018 (black), shaded areas indicate the standard error. (D-F) show temperature binned isoprene, monoterpene and sesquiterpene**
277 **fluxes respectively. The dashed lines depict the theoretical temperature behavior based on Guenther et al. (1993) (G93) and**
278 **Guenther et al. (1994) (G94) normalized to the respective fluxes at 303.15K.**

279 ### 3.3 Isoprene flux anomaly

280 The isoprene flux difference measured between the two summers of 2015 and 2018 is shown in Figure 2
281 A and D. Figure 2D represents the isoprene dependence on temperature. (Guenther et al. 1993). Monson
282 and Fall (1989) found isoprene fluxes not only to depend on current temperature conditions, but also on
283 current light conditions. In addition, past 24h and 240h temperature and light conditions play a role (e.g.
284 Guenther et al., 2006). These theoretical temperature and light parameters are plotted vs. the observed
285 isoprene flux in Figure 3A based on the MEGAN big leaf approach (Guenther et al., 2006). Even after
286 including both actual and past temperature and light parameters the difference in isoprene emissions
287 between the two summers could not be resolved and standardized emission factors were still a factor 2.4
288 higher in 2018 than in 2015. Figure 3B shows that the difference was increasing with higher
289 temperature and higher PAR values.
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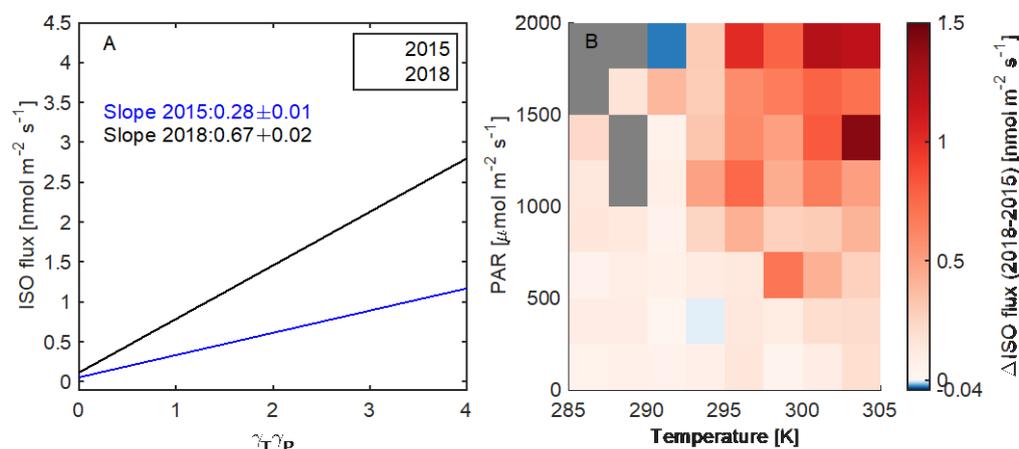
291
292 **Figure 3: A) Theoretical temperature and light dependencies (Guenther et al. 2006) including T24, T240, P24, P240 vs. observed**
293 **isoprene flux in 2015 (blue) and 2018 (black). The lines indicate a linear fit with fit parameters displayed within the plot. The slope**
294 **of the fit parameter represents the standardized (303.15 K and 1000 PAR) isoprene emission factors. B) Isoprene flux differences**
295 **between 2018 and 2015 binned by temperature and PAR, positive differences are shown in red, negative in blue and bins with no**
296 **available data are colored grey.**

297
298 In contrast to monoterpene and sesquiterpene emissions, which exhibited comparable emission
299 potentials between the two years and are mainly driven by evaporative emissions from storage
300 reservoirs (e.g. Kesselmeier and Staudt, 1999), it remains a puzzle why the isoprene emission potential
301 was substantially higher in 2018 compared to 2015. As neither actual temperature and light
302 dependencies nor 24h and 240h past temperature and light could explain the observed differences in

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303 isoprene fluxes, we investigated the following potential reasons: a) variation in the flux footprint, b) tree
304 trimming, c) water availability/drought, and d) emission parameterization.

305   a) As shown in Figure 1A the footprint area in 2018 was smaller than the footprint in 2015.
306   Possible reasons for this are a change in flux tower position between the two years by ~50 m, as
307   well as different meteorological conditions. Median wind directions were 71° and 68° and wind
308   speeds 1.6 m/s and 1.8 m/s in 2015 and 2018 respectively. The median Obukhov length was -26
309   m and -49 m in 2015 and 2018 respectively. Multiplying the footprint density at each tree
310   location with the basal emission factor of each tree species revealed a potential difference of
311   24% higher isoprene emissions in 2018 than in 2015. Even though the actual leaf area of each
312   individual tree is not known and therefore neglected, this 24% of potential emission difference
313   due to footprint changes cannot explain the factor of 2.4 in observed emissions between the two
314   years. This analysis assumes that the trees from the tree inventory were responsible for the
315   majority of isoprene emissions and that they were more important than emissions from short
316   vegetation (e.g. lawn). Further supporting evidence that the flux footprint change cannot fully
317   explain the observed differences derives from the fact that both monoterpenes and
318   sesquiterpenes did not show significant inter-annual variations in their normalized emission
319   potentials.

320   b) A second possible explanation for the isoprene flux difference could be that trees underwent
321   different trimming in the growing seasons which could lead to a different LAI in the two
322   seasons. Personal communications from city gardeners revealed that of the trees most important
323   for isoprene emissions in the study area (*Populus nigra*, *Populus alba*, *Quercus robur*) only
324   poplar trees were cut differently in 2015 than in 2018. In 2015 only dead wood was removed
325   from the poplars, whereas trees were cut more substantially in 2018. This would however lead to
326   an expected smaller flux in 2018 than in 2015 due to reductions in leaf area.

327   c) A third possible explanation is that the growing season of 2018 was exceptionally dry with
328   lower-than-average precipitation and satellite-derived rootzone soil moisture (Figure 4A and
329   4B). Concurrent water flux observations, however, shown in Fig. 4C, indicate that on average
330   the 2018 daytime summer water flux was 0.2 mmol m^{-2} s^{-1} higher than in 2015. Also the total
331   surface water vapor conductance was 50 mmol m^{-2} s^{-1} higher in 2018 than in 2015. Higher water
332   fluxes observed in 2018 agree with anecdotal reports of city trees being artificially watered
333   throughout the summer. Water fluxes in urban areas (maximum Bowen ratios observed in
334   Innsbruck: 6 (Karl et al., 2020)) are generally very low (e.g. 5-6 times lower) when compared to
335   measurements over purely vegetated surfaces, and therefore notoriously difficult to interpret. As
336   such we cannot exclude the possibility of processes other than evapotranspiration from city trees
337   contributing to higher water fluxes observed in 2018. An obvious explanation is that a
338   significant water runoff during extensive watering operations resulted in increased evaporation
339   over hot asphalt and other non-vegetated surfaces, leading to higher water fluxes in 2018. Water
340   was also applied to asphalt surfaces more frequently during mornings to minimize the effect of
341   urban aerosol pollution.
342   It is well established that isoprene production in plants can decouple from photosynthesis during
343   periods of drought and can be sustained by alternative metabolic carbon sources (e.g. Bertin &
344   Staudt, 1996; Pegoraro et al., 2004a,b; Fortunati et al., 2008; Genard-Zielinski et al., 2014;

345   Potosnak et al., 2014; Wu et al., 2015). The exact reason for biochemical regulation of isoprene
346   emissions during drought is not fully unraveled, but has been suggested to represent a response
347   for coping with heat stress (Loreto et al., 1998). Isoprene fluxes were observed to increase
348   during the very early onset of drought conditions. For example, Seco et al. (2015) reported an
349   increase in the ecosystem scale isoprene emission potential about one month before significant
350   changes in pre-dawn leaf water potential were observed, but when CO_2 uptake was already
351   decreasing. Additionally, they observed that the closing of stomata had a bigger effect on CO_2
352   than water fluxes, because gradual increases of vapor pressure deficit during the evening offset
353   reduced leaf conductance. Isoprene is not controlled by stomata and would not be influenced by
354   any changes in stomatal opening. In addition, their canopy scale observations suggested a shift
355   of the temperature maximum of isoprene emissions towards higher temperatures from pre-
356   drought to drought conditions. Ferracci et al. (2020) reported a threefold increase in the isoprene
357   emission potential during the same 2018 heat wave in a UK oak forest. They also observed a
358   stronger temperature dependence of isoprene emissions during the heat wave. We speculate that
359   the 50-60% increase of the isoprene emission potential observed here, could have similar
360   reasons, but this remains to be confirmed by detailed leaf gas exchange experiments.

361   d)   We also examined the impact of emission parameterization on isoprene emissions. Due to the
362   lack of soil water content data, which would be hard to interpret in an urban context, the drought
363   effect was not included in the emission model parameterization. Precipitation (Fig. 4A) and soil
364   moisture data (Fig. 4B) suggest 2018 being drier than 2015, corresponding to a significant heat
365   wave in the summer of 2018. Mild to severe drought conditions would reduce isoprene
366   emissions further and therefore could not explain an increased isoprene emission potential in
367   2018. The fact that evaporative water fluxes however were comparable between 2015 and 2018
368   (and if at all were somewhat higher in 2018), suggest that the trees might not have undergone a
369   severe drought episode in both years. To investigate relative changes in modelled emission
370   parameterizations we set up the MEGAN 5-layer canopy model (Guenther et al., 2006) for
371   different scenarios. We observed that a shift in T_{opt} towards higher temperatures helped
372   minimize the observed difference between the two years (e.g. 10% to 40%). As an example, the
373   diurnal daily isoprene flux differed between 2015 and 2018 by a factor of 3.8, and the 5 layer
374   model with T_{opt} set to 313 K could explain about half of the flux enhancement. This would leave
375   isoprene emission fluxes underestimated by about 50% in 2018.

376 In contrast to isoprene, temperature dependence algorithms accurately predict increases of
377 monoterpenes and sesquiterpenes due to increased temperatures in 2018 compared to 2015 (Fig. 2. B,
378 C). This can be rationalized by the fact that monoterpenes and sesquiterpenes are primarily released
379 from storage pools (Kesselmeier and Staudt, 1999), and temperature dependent changes in vapor
380 pressures of these compounds are accurately predicted between 2015 and 2018.
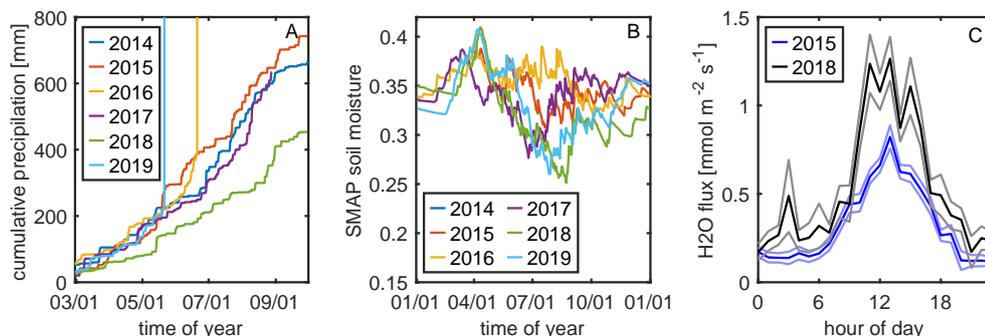
381
382 **Figure 4: A) cumulative precipitation for the growing seasons of 2014-2019 B) annual SMAP satellite soil moisture of the rootzone**
383 **from 2014-2019. C) diurnal cycle of water fluxes measured in 2015 (blue) and 2018 (black).**

3.4 Top-down and bottom-up BVOC flux ratios

385 Standardized flux ratios were calculated to allow for a better comparison with bottom-up estimates
386 based on literature values of branch level emissions and a city tree inventory. Top-down (eddy
387 covariance) ISO_S/MT_S ratios were on the order of 5 in 2015 and 12 in 2018, again revealing a strong
388 difference between the two years. Top-down MT_S/SQT_S flux ratios were in the order of 30-40 before
389 factoring in losses of sesquiterpenes due to reactions with ozone. Factoring in the upper bound of
390 chemical loss correction, MT_S/SQT_S flux ratios could have been as low as 12-16. Top-down ISO_S/SQT_S
391 flux ratios lay on the order of 190 in 2015 and 380 in 2018, which was mostly caused by the difference
392 in ISO_S flux between the two years. The lower bounds of the ISO_S/SQT_S flux ratios due to fast reaction
393 of sesquiterpene with ozone were 80 and 150 for 2015 and 2018, respectively.
394 Branch-level standardized emissions are collected from the literature in Table 1 and are used to
395 calculate a bottom-up emission map shown in Figures 5 A-C. The 2018 footprint area (Fig. 1A) and
396 therefore footprint density was different to 2015. Combining bottom-up emission estimates with
397 footprint density functions, the theoretically expected ISO/MT, MT/SQT and ISO/SQT ratios in 2015
398 were 3.6, 5.1 and 18.7 respectively. Applying the 2018 footprint density, the values were slightly
399 different with 4.2, 4.6 and 19.2 for ISO/MT, MT/SQT and ISO/SQT ratios respectively.
400 The bottom-up ISO/MT emission ratio was close to the top-down ratio of 2015. This indicates again
401 that 2018 was an exceptional year. In contrast, the bottom-up MT/SQT and ISO/SQT emission ratios
402 were significantly lower than both summers top-down measured flux ratios. Even after accounting for
403 the chemical loss of sesquiterpene before it reached the point of measurement at the top of the building,
404 the bottom-up estimates were still higher than the top-down measured flux ratios. Literature values for
405 leaf level sesquiterpene emissions are rare and were for many species estimated in Table 1. Further
406 extensive studies on sesquiterpene standardized emissions for a large variety of plant species is needed
407 to close the gap between bottom-up and top-down emission ratio estimates.

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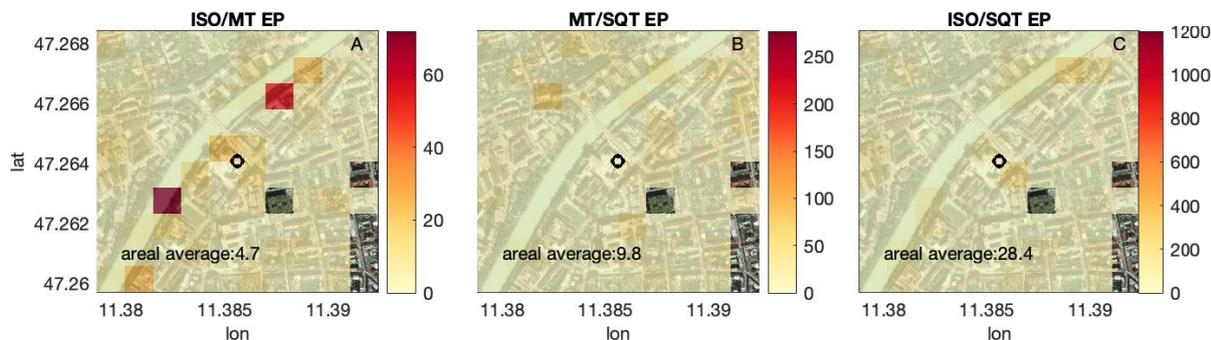
Figure 5: A-C Bottom-up estimates of standardized ISO/MT, MT/SQT and ISO/SQT emission ratios based on literature values (see Table 1). Maps were created in Matlab (www.mathworks.com) and are based on OpenStreetMap (https://www.openstreetmap.org/copyright) under the CC BY 3.0 AT license.

4 Summary

In this study we found a strong correlation of isoprene fluxes with temperature as well as isoprene fluxes following the previously observed leaf-level light dependency. A correlation between isoprene and benzene fluxes in early spring before the start of the vegetation period can be extrapolated to the summer months. This resulted in a maximum of 20-30% influence of anthropogenic sources on isoprene emissions during both 2015 and 2018 summer measurement periods. A PMF analysis at this site (Karl et al. 2018) revealed two biogenic factors: one light- and temperature-dependent for isoprene and a second mostly temperature-dependent including monoterpenes and sesquiterpenes. The here presented temperature dependency of monoterpene and sesquiterpene fluxes reveals a potential anthropogenic source at temperatures lower than 295K as the fluxes below this temperature lay above the predicted temperature curves based on leaf level measurements (Guenther et al. 1994). Bottom-up emission estimates based on a city tree inventory and emission factors from literature showed a reasonable agreement to standardized ISO/MT flux ratios and an underestimation of standardized MT/SQT and ISO/SQT flux ratios. As there are only few literature values for laboratory-based standardized sesquiterpene emissions, this discrepancy motivates further studies to be able to resolve this gap between bottom-up and top-down emission ratios.
Interannual comparison of biogenic fluxes revealed up to four times higher isoprene fluxes in 2018, when a heat wave persisted, than in 2015. Monoterpene emissions were an order of magnitude lower than isoprene emissions and sesquiterpene emissions were another order of magnitude lower than monoterpene emissions, however both summer emissions were comparable for these two terpenoid classes after standardization of temperature. Normalizing isoprene fluxes to standard light conditions did not fully remove the interannual difference but decreased the factor to 2.4. The difference increased with higher temperature and higher PAR values. Analysis of footprint, water availability and pruning activity differences of the two summers did not resolve the observed differences in isoprene fluxes. Detailed analysis using standard emission modeling concepts suggested a higher-than-expected variation of urban isoprene emission potentials during the heat wave in 2018. While water flux

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measurements did not indicate a severe drought in 2018, the effect of an intense heatwave in 2018 (2K higher temperatures on average compared to 2015), likely resulted in enhanced isoprene emissions. Isoprene emissions during drought stress have been grouped into two distinct phases (Niinemets, 2010, Potosnak et al., 2014), and can be enhanced under pre-drought conditions (Seco et al., 2015, Ferracci et al., 2020). Enhanced leaf temperatures (e.g. Potosnak et al., 2014) can explain part of the variance in isoprene emissions, but significant differences remained. In addition to the leaf temperature effect, Tattini et al., (2015) reported an upregulation of isoprene emissions during drought stress as antioxidant defense in *Platanus x acerifolia* plants. If generalized, our observations could suggest distinct differences that urban trees experience, possibly due to significantly altered environmental conditions (e.g. stresses, light and temperature environment), which standard big leaf models might not fully capture. Vegetation in urban areas is exposed to a variety of different atmospheric conditions, for example the urban heat island effect, high levels of NO_y, heavy metal deposition or high loadings of aerosols (e.g. black soot). Isoprene emissions have been linked to the plant's nitrogen metabolism (e.g. Rosenstiel et al., 2008), where higher leaf nitrate can lead to lower isoprene emissions. Nitrogen dioxide concentrations have been falling in Innsbruck and were 20% lower in 2018 than in 2015. Effects of air pollutants on leaf surface characteristics and senescence were also reported in the past (Jochner et al. 2015; Honour et al., 2009), but a quantitative understanding of the impacts on isoprene emissions remains unclear. Our observations suggest that more work is needed to improve our understanding of urban biogenic isoprene emissions.

Acknowledgements

Conflict of Interest

There is no conflict of interest.

Code and Data availability

The eddy covariance flux code used to analyze fluxes can be accessed via Github (https://git.uibk.ac.at/acinn/apc/innflux). Data can be shared upon request.

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Author contributions

LK and TK designed and conceived the manuscript. MG was leading the instrumental operation of the PTR-TOF-MS for the 2015 and 2018 campaigns. MG, SJ, AP and MS performed the raw data processing of NMVOC data. MS, TK and MG performed the NMVOC flux analysis. GW provided input on tree species information. TK and LK performed analysis regarding BVOC emission modeling. SJ aided in the operation of the PTRTOFMS and raw data processing of NMVOC data for the 2018 campaign. All authors provided input and contributed to writing the manuscript.

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Table 1. Literature values of the 44 most abundant tree species found in the 1 km² area surrounding the measurement site. All values are given in mg g(dry weight)$^{-1}$ h^{-1}. Reference subscripts refer to a) Stewart et al., 2003, b) Kesselmeier & Staudt 1999, c) Karl et al. 2009, d) Noe et al. 2009, e) Nowak et al. 2002, f) Wang et al 2007, g) Baghi et al 2012, h) Li et al 2009, i) Owen et al. 2003, *) standard value of 0.1, as no literature value available.

plant species name	number of trees	ISO emission potential	MT emission potential	SQT emission potential
Acer platanoides	202	0.02[a]	1.83 [a]	0.1[c]
Betula pendula	151	0.05[a]	2.80 [a]	2[c]
Aesculus hippocastanum	98	0.10[a]	0.10 [a]	0.1[*]
Fagus sylvatica	97	0.01[a]	0.36 [a]	0.1[c]
Fraxinus excelsior	90	0.00[a]	0.00 [a]	0.1[c]

Prunus avium	85	0.10[a]	0.24[a]	0.1[c]
Robinia pseudoacacia	85	11.87[b,c,d]	2.48[b,c,d]	0.1[c]
Acer pseudoplatanus	77	0.00[a]	0.00[a]	0.1[c]
Picea abies	68	1.07[a]	4.00[a]	0.1[c]
Pinus sylvestris	68	0.10[a]	6.45[a]	0.1[c]
Tilia platyphyllos	54	5.50[a]	0.10[a]	0.1[c]
Taxus baccata	52	0.10[a]	0.10[a]	0.1[*]
Cornus mas	40	0.10[e]	1.60[e]	0.1[*]
Populus alba	40	53.00[a]	2.30[a]	0.1[c]
Prunus cerasifera	37	0.10[a]	0.79[a]	0.1[*]
Quercus robur	36	38.45[a]	0.94[a]	0.1[c]
Populus nigra	35	52.50[a]	2.30[a]	0.1[c]
Cupressus sp	32	0.10[a]	0.90[a]	0.1[c]
Carpinus betulus	30	0.10[a]	0.04[a]	0.1[c]
Acer campestre	29	0.05[a]	0.10[a]	0.1[c]
Salix alba	24	37.20[a]	1.10[a]	0.1[c]
Platanus acerifolia	22	20.00[a]	0.05[a]	0.1[*]
Tilia cordata	21	0.00[a]	0.00[a]	0.1[c]
Prunus serrulata	18	0.10[a]	0.79[a]	0.1[*]
Acer saccharinum	17	0.10[b]	2.85[b,c]	0.1[*]
Cupressus sempervirens	15	0.00[c]	0.70[c]	0.1[c]
Abies alba	14	1.00[c]	1.50[c]	0.1[c]
Pinus cembra	14	0.00[c]	2.50[c]	0.1[c]
Sophora japonica	14	10.00[f]	0.10[f]	0.025[*]
Thuja occidentalis	14	0.00[c]	0.60[c]	0.025[c]
Ginkgo biloba	11	0.30[h]	0.60[h]	0.025[*]
Malus domestica	11	0.50[a]	0.60[a]	0.025[c]
Sorbus aucuparia	11	0.50[a]	0.10[a]	0.025[c]
Gleditsia triacanthos	10	0.10[e]	0.70[g,e]	0.025[*]
Sorbus intermedia	10	0.50[a]	3.00[a]	0.025[*]
Aesculus	8	0.00[g]	12.00[g]	0.025[*]

carnea				
Chamaecyparis lawsoniana	8	0.10[i]	0.67[i]	0.025[*]
Liquidambar styraciflua	8	46.58[b]	19.17[b]	0.025[*]
Magnolia Kobus	8	0.05[a]	3.25[a]	0.025[*]
Platanus hispanica	8	20.00[a]	0.05[a]	0.025[*]
Acer palmatum	7	0.05[a]	1.83[a]	0.025[*]
Juglans regia	7	0.00[b]	1.40[b, c]	0.025[c]
Larix decidua	7	0.00[c]	5.00[c]	0.025[c]
Platanus occidentalis	7	20.00[a]	0.05[a]	0.025[c]

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