Interannual Variability of ~~BVOC~~ Terpenoid Emissions in an Alpine City

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Abstract. Terpenoid emissions above urban areas are a complex mix of biogenic and anthropogenic emission sources. In line with previous studies we found that summertime terpenoid fluxes in an alpine city were dominated by biogenic sources. Inter-seasonal emission measurements revealed consistency for monoterpenes and sesquiterpenes, but a large difference in isoprene between the summers 2015 and 2018. Standardized emission potentials for monoterpenes and sesquiterpenes were 0.12 nmol m^{-2} s^{-1} and 3.0 x 10^{-3} nmol m^{-2} s^{-1} in 2015 and 0.11 nmol m^{-2} s^{-1} and 3.4 x 10^{-3} nmol m^{-2} s^{-1} in 2018, respectively. Observed isoprene fluxes were almost three times higher in 2018 than in 2015. This factor decreased to 2.3 after standardizing isoprene fluxes to 30°C air temperature and photosynthetic active radiation (PAR) of 1000 µmol m^{-2} s^{-1}. Based on emission model parameterizations, increased leaf temperatures can explain some of these differences, but standardized isoprene emission potentials remained higher in 2018, when a heat wave persisted. These data suggest a higher variability of interannual isoprene fluxes than for other terpenes. Potential reasons for the observed differences such as emission parameterization, footprint changes, water stress conditions and tree trimming are investigated.

~~**Abstract. Terpenoid emissions above urban areas are a complex mix of biogenic and anthropogenic emission sources. In line with previous studies we found that summertime terpenoid emissions fluxes in an alpine city were dominated by biogenic sources, but especially at lower temperatures the anthropogenic influences were non-negligible. Inter-seasonal emission measurements revealed consistency for monoterpenes and sesquiterpenes, but a large difference in isoprene between the summers 2015 and 2018. Standardized emission potentials for monoterpenes and sesquiterpenes were 0.12 nmol m^{-2} s^{-1} and 3.0 x 10^{-3} nmol m^{-2} s^{-1} in 2015 and 0.11 nmol m^{-2} s^{-1} and 3.4 x $\cdot 10^{-3}$ nmol m^{-2} s^{-1} in 2018, respectively. Observed isoprene emissions~~

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1 Introduction

Biogenic and anthropogenic volatile organic compounds (BVOCs, AVOCs) in the atmosphere can contribute to surface air pollution both due to their influence on tropospheric ozone formation and due to their potential to act as precursors for secondary organic aerosol ~~formation~~ (Derwent et al., 1996, Fehsenfeld et al., 1992, Fuentes et al., 2000, Goldstein et al., 2009, Laothawornkitkul et al., 2009, Riipinen et al., 2012). BVOCs are playing a particularly important role globally, as their emission strength is estimated to be 10 times larger than AVOCs (Guenther et al., 2012, Piccot et al., 1992). Also, many BVOCs are characterized as highly reactive (Atkinson and Arey, 2003, Fuentes et al., 2000), resulting in rapid peroxy radical chemistry important for ozone and ultra-fine particle formation processes (Simon et al., 2020). Of the total global BVOC emissions, terpenes dominate, with 50% attributed to isoprene, 15% to monoterpenes and about 0.5% to sesquiterpenes (Guenther et al., 2012). In predominantly isoprene-emitting forests ~~In forests with predominating isoprene emissions,~~ isoprene was found responsible for 50-100% of the tropospheric ozone production (Duene et al., 2002, Tsigaridis and Kanakidou, 2002, Poisson et al., 2001). In coniferous forests monoterpene and sesquiterpene emissions often dominate (Johansson and Janson, 1993, Thunis and Cuvelier, 2000, Juráň et al., 2017). It has been shown that RO_2 self-reactions of monoterpenes and sesquiterpenes can rapidly create highly oxidized matter (HOM) and are a key player for new particle formation (NPF) events in forests under low NOx conditions (Simon et al., 2020).

In urban environments where the mixture of BVOCs and AVOCs is more complex, several recent studies point out the importance of biogenic emissions for local air quality (Simon et al., 2019, Bonn et al., 2018, Churkina et al., 2017, Ren et al., 2017, Papiez et al., 2009, Chameides et al., 1988) and that the BVOC influence is especially high during summertime heat waves (Churkina et al. 2017). Particularly in summer, biogenic sources are dominating in urban environments. E.g., Yadav et al. (2019) found an increased importance of biogenic isoprene in an urban site in western India during pre-monsoon season when temperatures and PAR were high, Hellen et al. (2012) found a strong biogenic influence on isoprene and monoterpene concentrations in Helsinki in July. Summertime isoprene in two large Greek cities was determined by PMF to mainly (60-70%) originate from vegetation ~~appointed with PMF to come 60-70% from vegetation~~ (Kaltsonoudis et al. 2016). Yang et al. (2005) showed a strong seasonal and daily cycle in isoprene, attributing it therefore~~isoprene contributing it therefore~~ to biogenic sources in an urban region in Taiwan. Borbon et al (2002) showed that biogenic sources strongly superimpose the traffic emissions of isoprene in summer in an urban area in France. Wagner and Kuttler (2014) found that during summer afternoons in an urban area in Germany anthropogenic influences on isoprene concentrations were negligible. Chang et al. (2014) and Wang et al. (2013) showed that in a tropical-subtropical metropolis biogenic contributions overwhelmed anthropogenic

contributions of isoprene in summer and that biogenic sources started to dominate in all seasons above a threshold temperature of 17-21°C. Whereas all the studies cited above ~~Whereas all so far cited studies~~ were based on concentration measurements where the influence can be both local and regional and strongly modulated by atmospheric dilution, the following studies were based on eddy covariance flux tower sites. ~~:~~ At temperatures over 25°C more than 50% of the isoprene flux was found to be biogenic in origin in London with a mean daytime flux of 0.18 mg m^{-2} h^{-1} (Langford et al. 2010). Similarly, Valach et al. (2015) in a different study in London found a mean daytime flux of 0.2 mg m^{-2} h^{-1}. Kota et al. (2014) found a daytime median flux of 2.1 mg m^{-2} h^{-1} over Houston, Texas and contributed it to mostly biogenic sources. Park et al (2010) found also in Houston, Texas a daytime isoprene flux of 0.7 mg m^{-2} h^{-1}. Rantala et al. (2016) found that 80% of the measured 10 ng m^{-2} s^{-1} summer daytime isoprene flux near Helsinki could be contributed to biogenic sources by comparing emissions at low and high temperatures.

While there is evidence for urban trees to have positive influence on urban environments such as mitigating the urban heat island effect, sequestering CO_2 and particles as well as via storm water interception ~~as well as acting as storm water interception~~ (Escobedo et al., 2011, Connop et al., 2016, Livesley et al., 2016), BVOC emissions of urban trees and their subsequent effect on air pollution are very plant-species dependent ~~is very plant species dependent~~ (Corchnoy et al., 1992, Steinbrecher et al., 2009, Fitzky et al., 2019) and should be taken into account when planting urban trees (Calfapietra et al., 2013, Churkina et al., 2015, Ren et al., 2017). Emerging evidence that isoprene derived RO_2 competes with RO_2 radicals from higher molecular weight terpenes in the formation of new particles highlights the need to study emissions in different environments (Berndt et al. 2018).

~~To assess the status quo of BVOC emissions in a city or area and their impact on local air quality urban eddy covariance flux measurements have become available for some urban areas (Langford et al. 2010, Park et al 2010, Kota et al. 2014, Valach et al. 2015, Rantala et al. 2016).~~

Few studies characterize the ~~seasonal and~~ interannual changes of BVOCs and even fewer such studies ~~even fewer studies~~ are available in urban environments. ~~: Chang et al. (2014) measured seasonal changes in urban isoprene concentrations in Taipei revealing the biogenic dominance of isoprene in daytime concentrations of biogenic sources for spring, summer and fall and even a dominance of biogenic sources at night in summer. Valach et al. (2015) showed decreasing isoprene fluxes transitioning from summer to winter at a central London measurement site.~~ Vaughan et al. (2017) report airborne flux measurements over South Sussex of two consecutive summers showing different isoprene ~~emissions~~ fluxes that can be explained by different temperature and cloud cover conditions. Warneke et al. (2010) tried to explain the measured interannual differences of a factor of 2 in ~~emissions~~ fluxes of isoprene and monoterpene over Texas by temperature, drought effects or influences from changes in leaf area index (LAI). Palmer et al. (2006) found a maximum of 20-30% interannual difference in isoprene emissions using satellite-based isoprene quantification from formaldehyde measurements over North America. A model study by Steinbrecher et al. (2009) found only a 10% annual difference in biogenic emissions from cold to hot years. Gulden et al. (2007) found that, on a regional scale, variations in leaf biomass density driven by variations in precipitation are together with temperature and shortwave radiation variations the most important factors for variations in BVOC emissions. Tawfik et al. (2012) found in a model study that interannual variation of isoprene emission is ~~with 18%~~ strongest in July with temperature and soil moisture explaining 80% of the variations, whereas the influences of

variations in photosynthetic active radiation (PAR) and LAI were negligible. In a three-year study over a northern hardwood forest, Pressley et al. (2005) found that total cumulative isoprene ~~emissions~~ fluxes varied only by 10%.

Given the current lack of multi-year urban VOC flux measurements and our limited understanding of the interannual variability of biogenic and anthropogenic emission sources, the objective of the present study was to quantify the interannual variation of the urban ecosystem-atmosphere exchange of the three major isoprenoids, isoprene, monoterpenes, and sesquiterpenes, and to analyze the underlying drivers. We hypothesized (i) that the exchange of these BVOCs can be attributed largely to the spatio-temporal variability of biogenic sources and (ii) that differences in environmental forcings are the main drivers of interannual variability. To address these hypotheses, urban eddy covariance BVOC flux measurements during two growing seasons above the city of Innsbruck (Austria) are blended with bottom-up emission estimates based on a process-based model and a detailed urban tree inventory.

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. The data record in 2018 is continuous, in 2015 the data record has a gap between July 31 and August 03. 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 21000x21000m map surrounding the site. ~~This will in the following be referred to as the study area.~~ The dominant wind direction at the IAO is from the NE during the daytime and from the 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 at a sampling frequency of 10 Hz on a tower on top of the building 42 m above street level. In 2015 the tower was at a provisional location at the north of the building; the heading direction of the sonic anemometer was 76°. Flow distortions for westerly winds due to the building and the support structure cannot be excluded. In the course of the establishment of the IAO lab the CPEC200 the inlets were moved ~50 m to the southern edge of the building with an anemometer heading of 129° and minimal flow disturbances. For comparability isoprenoid fluxes in this study are limited to the northeastern sector of [0°,120°] in both years.

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) , which allows for the acquisition of full, high-resolution mass-spectral information at 10 Hz. Residence time of air samples in the turbulently purged teflon inlet line (Teflon PFA, ¼" ID x 12.7m heated at 30°C) is about 0.4 seconds to keep wall loss and chemical transformation of isoprenoids negligible. 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) (PAR/short wave radiation ~0.46 during summer daytime conditions).
Precipitation data were collected 400 m south of our field site by a MPS TRWS 503 tipping bucket precipitation gauge (MPS TRWS 503) and a Thies 5.4103.10.000 precipitation monitor (Thies 5.4103.10.000), mounted at 1.5 m above a grass surface, both operated by Zentralanstalt für Meteorologie und Geodynamik (ZAMG, Austrian Met-Service) at the station Innsbruck Universität (WMO SYNOP number 11320).
Due to the lack of directly measured city-scale soil moisture data, pPlant 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/https://lpdaacsvc.cr.usgs.gov/appeears/). Due to the large spatial footprint of this product, the corresponding data will only be used to interpret interannual differences in precipitation on soil moisture.

2.2 Eddy covariance fluxes

This study focuses on biogenic emissions fluxes collected during summer 2015 and summer 2018. The presented eddy covariance flux measurements are used to constrain BVOC flux parameterizations. Biogenic emissions, in particular isoprene, are strongly light- and temperature-driven. As a consequence we selected daytime flux data. During daytime the flux footprint density points towards the east sector imposed by the local valley wind system. In order to test BVOC emission parameterizations we therefore selected daytime hours (06:00-18:009:00-16:00 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, for which we believe current footprint density calculations bear too much uncertainty in an urban setting. Eddy covariance fluxes were calculated using a MATLAB® code described by Striednig et al. (2020). Figure S1 shows the co-spectral response of the PTR-QiTOF-MS and inlet system. The loss of covariance of isoprenoids signals with vertical windspeed due to lowpass filtering is less than 4% (see Spectral analysis in Supplemental Information)
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. Implementing these QA/QC criteria reduced the available flux data by 29% and 11% in 2015 and 2018, respectively.
The Footprint and footprint density representing the relative contributions of an air mass sample arriving at the flux tower wasere calculated following Kljun et al. (2015).

Constraints on the lifetime of reactive terpenes: Turbulent time scales (100 s) can be the order of chemical time scales of some monoterpenes which can react fast with ozone. We calculate the chemical

loss by the following equation: $c(t)/c0=\exp(-t_{turb}/t_{chem})$ where t_{turb} is the turbulent time scale and t_{chem} the chemical time scale. The turbulent time scale was obtained from the ratio of the measurement height (H) over the friction velocity (H/u*). For typical turbulent time scales of 100 s, reaction with OH can be neglected.

Further, our analysis of emissions is primarily focused on the interpretation of daytime fluxes, when NO3 radical chemistry plays a minor role compared to ozone. Ozone follows the expected diurnal cycle for an urban area (30-50 ppbv mixing ratios). Since we do not have speciated terpene fluxes, we performed a sensitivity study (e.g. estimating realistic bounds) assuming a fraction of the total sesquiterpene (or monoterpene) flux was composed by the most reactive compound (rSQT and rMT). For sesquiterpenes, for example, we can take the estimated rate constant for ozone and beta caryophyllene: 1.2e-14 cm3/molecules/s. A typical compositional mix of sesquiterpenes was reported by Sakulyanontvittaya et al., 2008), who assessed reactive terpene fractions between 36-50%. Typical reaction rates of less reactive sesquiterpenes (nrSQT) (e.g. cedrene, longifolene: Atkinson et al., 1994) are on the order of 1 to 10 x 1e-17 cm3/molecules/s. Taking these boundary conditions gives a realistic range of the reacted fraction of measured SQT fluxes. Similarly we can do the analysis for monoterpenes, where the fraction of reactive terpenes (rMT) such as ocimene is typically lower (e.g. 10 - 15% - Sakulyanontvittaya et al., 2008,). For comparison, trans-beta-ocimene, one of the most reactive monoterpenes known to be emitted from plants, has a reaction rate constant of 2.6e-14 cm3/molecules/s. Figure S2 and S3 in the supplemental information show the non-reacted flux for total sesquiterpenes due to reaction with ozone assuming a 36 to 64 and a 50 to 50 mix (rSQT to nrSQT). With these scenarios daytime reductions of total sesquiterpenes fluxes due to chemistry would be on the order of 30-45%. For monoterpene fluxes we calculate losses on the order of 12% (Figure S4).

2.3 Emission standardization of fluxes

Big leaf model for standardization of surface fluxes: We standardized isoprene eddy covariance fluxes $E_{0,ISO}$, to a temperature of 303.15 K and PAR of 1000 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 γ_T and γ_P are temperature- and light-dependent coefficients respectively containing current and past (24h and 240h) conditions.

Monoterpene and sesquiterpene emissions are often dominated by temperature. Originally the temperature dependence has been 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 dependent factor (e.g. Guenther et al. 1994). Some monoterpene and sesquiterpene emissions have also been reported to be produced de novo and can therefore show a light dependent emission behavior (e.g. Staudt and Seufer, 1995). The light dependent portion is included in updated emission algorithms (e.g. Guenther et al., 2012, equation 3-6), where the light dependent portion is modeled in analogy to isoprene, and the light independent fraction is incorporated according to Guenther et al. 1994. The light dependent fraction for monoterpenes varies between 0.2 and 0.8, and for sesquiterpenes it is currently assumed to be 0.5. The temperature and light parameterization was calculated using equation 3 - 11 from Guenther et al., (2012) who prescribed a 50% light dependent fraction for SQT emissions. For Monoterpenes we take the average light dependent fraction from Guenther et al., 2012 (i.e. 50%), since we do not have speciated MT fluxes.

MEGAN 5 layer model: In order to investigate the sensitivity of isoprene emissions to the emission model framework we also setup a 5 layer canopy model according to Guenther et al. (2006). The setup was used to conduct a sensitivity experiment to study potential inter-seasonal changes in isoprene

emissions between 2015 and 2018 based on different model formulations. For the sensitivity run the model was constrained by measured radiative fluxes, sensible and latent heat fluxes. We prescribed a LAI of 1 to account for sparse vegetation and mimic a sunleaf dominated scenario, with a mean sunlit fraction of 64% (40-95%).

Direct LAI measurements are not available for this study. Both campaigns were conducted in similar time frame within the year which should lead to comparable leaf age. No early senescence in either year was reported by the city gardeners.

2.4 Bottom-up emission potentials

City tree inventory: An inventory of all trees planted by the city municipality is available for the city of Innsbruck, Austria containing location, tree species, diameter at breast height and height. However, this inventory does not include trees from private gardens. Therefore, all accessible trees from private gardens were identified and added to the existing tree inventory in an area 1000x1000m surrounding the observatory. This will in the following be referred to as the study area.. The location of the trees from the city inventory (41 %) and private gardens (59 %) in the study area are shown in Figure 1A. Within the study area a total of 1904 registered trees distributed across 129 tree species were counted and it is estimated that these cover > 90 % of the available trees . A list of the 44 most abundant tree species, where the species count in the study area was 6 or more, is given in Table 1.

Emission potentials: Literature values of plant-species specific emission potentials of isoprene and monoterpene, in µg compound g^{-1} dry-weight h^{-1} standardized to 303.15 K and PAR 1000 µmol m^{-2} s^{-1} were assigned to the 44 most abundant species in the study area. This includes all tree species with an occurrence larger than 6 individuals within the 60% footprint density and accounts for ~90% of the total counted trees. Emission potential assignment was based, if available, on the detailed work by Stewart et al. (2003) ~~for the overlapping species~~. Other emission potentials were taken from other literature and if more than one literature value was available, an average was taken. All species, emission potentials and references thereof are shown in Table 1. Sesquiterpene (SQT) emission potentials were taken from Karl et al. (2009) and if not reported therein the average value of 0.1 µg compound g^{-1} dry-weight h^{-1} was assigned.

2.5 Relative ISO, MT, SQT emission ratio maps

To generate emission ratio maps, the study area was divided into a 100 m by 100 m grid and tree species were counted in each grid tile and multiplied by their emission potential listed in Table 1. The resulting map in units of µg compound g^{-1} dry-weight h^{-1} neglects the actual, but unknown, amount of dry leaf weight of each individual tree.
Due to the unknown amount of emitting leaf material, it is difficult to compare bottom-up estimates from this method with direct eddy covariance flux measurements. A more robust comparison is possible when relative emission maps are investigated such as ISO/MT, ISO/SQT and SQT/MT. For this we first added up all individual tree emission factors in each tile (e.g. $ISO_{tile} = \sum ISO_{tree}$) and then divided

these by the tile emission factors e.g. ISO_{tile}/MT_{tile}. For simplicity this is in the following called ISO/MT. This is a bottom-up ISO/MT ratio expected at the measurement site. The authors acknowledge that leaf age, phenology, and LAI or individual trees affect this ratio but both are unknown for the tree inventory and are therefore a source of uncertainty of this estimate. Doubling and halving the emission potential of the highest 20 emitters resulted in average study area emission ratios changes on the order of 5-15% giving an estimate of the robustness of this analysis.

3 Results and discussion

3.1 Flux footprint, light & temperature conditions

The flux footprint density ~~of the daytime data~~ at the IAO is shown in Figure 1A and 1B for 2015 and 2018, respectively. Flux footprint density lines from 30-90% are plotted on a map of 2~~1~~000 m x 2~~1~~000 m surrounding the flux tower location. 60% of the flux footprint density lay, in both years, entirely within the study area (1000 m x 1000 m). ~~The footprint area extended slightly farther in 2015 than in 2018.~~ The relative contribution of the land cover types within the study are ~~in both years however~~ was similar in both years with 40-41% buildings, 23% paved areas, 25-28% roads, 5% trees, 5% short vegetation, and <1% water. Within the 60% flux footprint density area in 2015 and 2018 lay 148 and 89 individual trees of the tree inventory distributed over 33 and 24 tree species, respectively. Combining the tree inventory with literature values on basal emission factors (Table 1) and the footprint density calculated for each tree location revealed that 60% and 70% of the bottom-up isoprene emissions arriving at the flux tower were from 12 trees in 2015 and 2018 respectively. These were trees closest to the footprint density maximum and trees with high isoprene basal emission factors. The tree species were *Populus nigra*, *Platanus acerifolia*, *Sophora japonica*, and *Quercus robur*. As the 60% footprint density area was smaller in 2018 compared to 2015, the relative importance of the emission of these trees was higher in 2018 than in 2015. Bottom-up monoterpene emissions were distributed more evenly among different tree species: 19 trees in the study area accounted for ~50% of the bottom-up MT emissions arriving at the flux tower. The most important species were *Aesculus carnea*, *Pinus sylvestris*, *Larix decidua*, and *Acer platanoides*. Sesquiterpene bottom-up emissions were even more equally distributed over the tree species: 38 trees accounted for 50% and 60% of bottom-up SQT emissions arriving at the flux tower in 2015 and 2018 respectively. *Betula pendula* and *Sophora japonica* contributed 20% and 12% to the emissions arriving at the tower in 2015 and 22% and 19% in 2018. Diurnal cycles of PAR and air temperature, two of the strongest biogenic emission drivers, are shown in Figure 1C~~B~~ and 1D~~C~~, respectively. While PAR was very similar during the two summers, mean air temperatures in 2018 were 2K higher during daytime and 1.5K higher during nighttime compared to 2015. The higher temperatures in 2018 coincided with an intense heat wave. Monthly average temperatures in August 2018 were 3K above the climatological mean values (1981-2010).

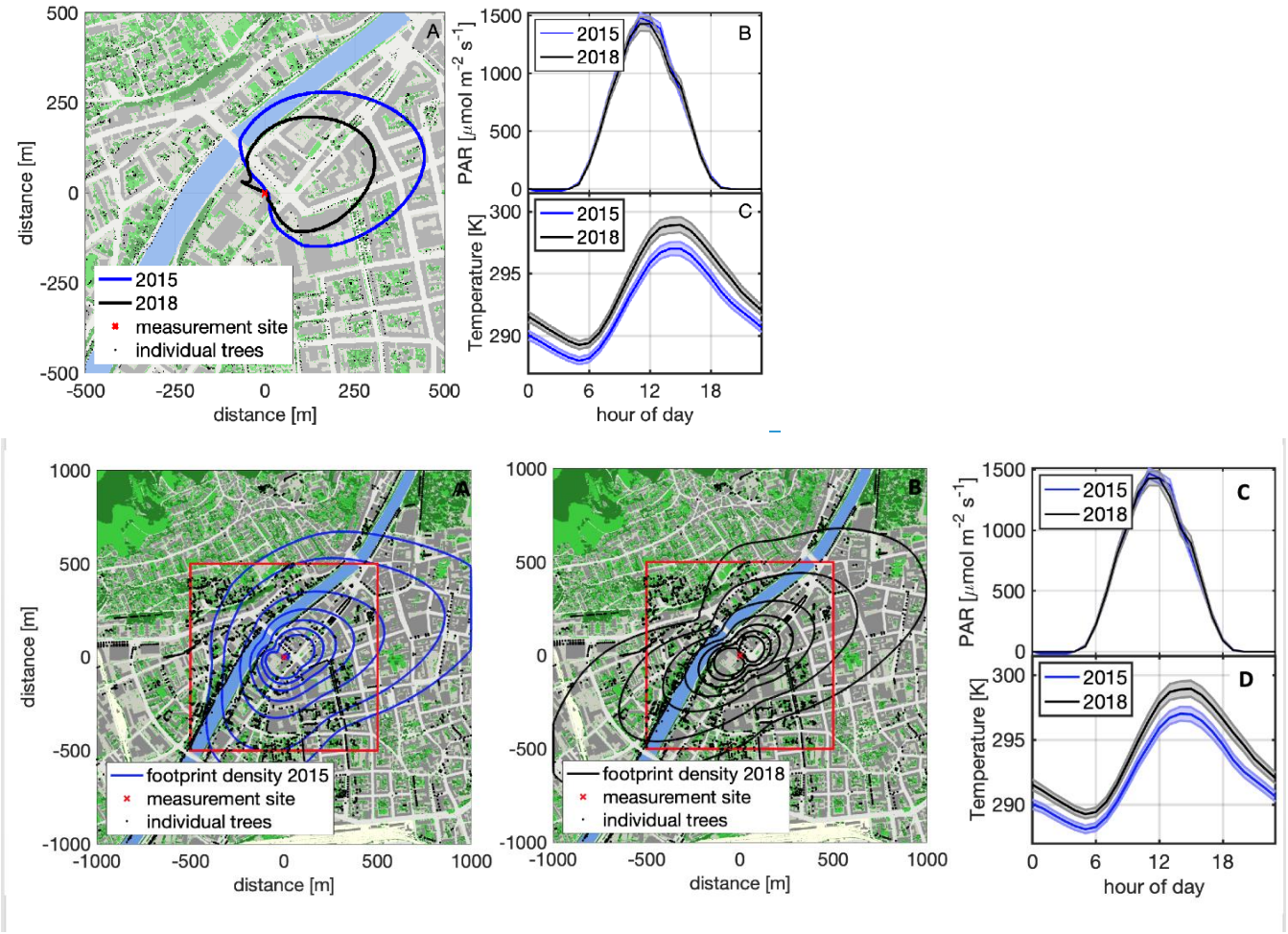


Figure 1: A) Map surrounding the Innsbruck Atmospheric Observatory (indicated with a red cross in the center) depicting trees, short vegetation, water, roads, paved areas and buildings in dark green, light green, blue, white, light grey and dark grey respectively. Black dots represent individual trees from the city tree inventory. The study area is indicated with the red rectangle. 2015 footprint density lines from 30%-90% are plotted as blue lines ~~daytime (06:00-18:00) footprint areas with mean wind directions between 0° and 120° are shown in blue and black for summer 2015 and 2018 respectively~~. B) Same as map as A with 2018 footprint density lines in black. C) Diurnal cycle of average and standard error of PAR in 2015 (blue) and 2018 (black). D~~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~~ isoprenoid 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 show~~s~~ the average diurnal cycles of isoprene, monoterpene and sesquiterpene fluxes. Mean d~~D~~aytime maxima of isoprene ~~emissions~~ fluxes were 0.4 nmol m^{-2} s^{-1} and

1.2 nmol m^{-2} s^{-1} in 2015 and 2018 respectively. The large interannual difference and its potential reasons are discussed further in section 3.3. Anthropogenic contributions to isoprene emissions from traffic were on the one hand estimated using the COPERT emission model (https://www.emisia.com/utilities/copert/) and 1,3 butadiene as a proxy. We use the ratio of 1,3 butadiene to isoprene from road tunnel studies (Reimann et al., 2000) and multiply this to the modeled 1,3 butadiene to benzene ratio. There is no significant modeled difference between warm and cold seasons because unsaturated hydrocarbons as well as benzene primarily originate from combustion related emissions. Relative to benzene we calculate that anthropogenic isoprene emissions contribute on the order of 5% during daytime (Fig. S5 for the summer season. At night the contribution can be larger (e.g. up to 20%) as biogenic emissions decrease more rapidly than benzene fluxes. On the other hand we used the measured winter-time isoprene/benzene flux ratio, which revealed a conservative limit of 20% due to anthropogenic origin. Overall isoprene emissions are dominated by biogenic emissions at this site. This is in good accordance with previous studies conducted in urban environments (Kota et al. 2014, Park et al 2010, Rantala et al. 2016).

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 x 10^{-3} nmol m^{-2} s^{-1} in both years.

The theoretical temperature and light parameters are plotted vs. the observed fluxes in Figure 2 D-F based on the MEGAN big leaf approach (Guenther et al., 2006, Guenther et al., 2012.). The slope of the fit parameters represents the standardized (303.15 K and 1000 PAR) emission factors. The slopes in Fig. 2. D-F can be interpreted as standardized fluxes, removing the variability due to current and past temperature and light conditions and allows for interannual comparison as well as comparison to other studies. Standardized isoprene fluxes were 0.26±0.02 nmol m^{-2} s^{-1} and 0.67±0.02 nmol m^{-2} s^{-1} in 2015 and 2018 respectively. The interannual difference is further discussed in section 3.3. Isoprene fluxes from both years were lower than what Rantala et al. (2016) found for an urban flux site in Helsinki, where the standardized emission potential was 125 ng m^{-2} s^{-1} (eq. to: 1.8 nmol m^{-2} s^{-1}). The Helsinki flux site had a larger vegetation cover of 38-59% compared to our study area, where the vegetation cover was estimated to be 10% within the flux footprint. Park et al. (2010) reported a 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, which is higher than both our 2018 and 2015 measurements. This is potentially due to a higher vegetation cover in Houston as well as strong isoprene-emitting oaks within the footprint of the measurement site. Valach et al. (2015) reported a daytime average flux in August of 0.3 mg m^{-2} h^{-1} (eq. to: 1.2 nmol m^{-2} s^{-1}) at an urban site in London and Acton et al. (2020) a summer daytime average isoprene flux of 4.6 nmol m^{-2} s^{-1} at an urban site in Beijing, both however cannot be directly compared to our measurements as their values were not standardized to temperature and PAR.

Average daytime standardized monoterpene fluxes were, with 0.04 and 0.05 nmol m^{-2} s^{-1} in 2015 and 2018, respectively, relatively similar between the two summers. Average daytime standardized sesquiterpene fluxes were over a magnitude smaller than standardized monoterpene fluxes and were comparable between the two summers with mid-day values on the order of 3.0 x 10^{-3} nmol m^{-2} s^{-1} and 3.5 x 10^{-3} nmol m^{-2} s^{-1} in 2015 and 2018 respectively. Both monoterpene and sesquiterpene flux

measurements could be underestimated due to loss with reaction to ozone. The values given here could be underestimated by 10% for monoterpenes and 35-45% for sesquiterpenes (see section 2.2).
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. MMeasured monoterpene and sesquiterpene measured fluxes measured at lower temperatures (280K-295K) were higher than the predicted values based on biogenic emission parameterizations (data not shown). 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. To test this hypothesis we considered footprint variations and relative distributions between grasses and trees, which were minor. Variations in flux footprint and a relative distribution with higher grassland MT emissions can be excluded as an explanation for MT and SQT excursions. Instead we find that the residual of non-explained MT and SQT fluxes correlates well with aromatic fluxes. We find a significant positive correlation (R2 ~0.75; RMSE: 0.006204) of the residual MT flux with the benzene flux (Fig S5). It suggests that emission of volatile chemical products (VCPs) (e.g. Gkatzelis et al. 2021) is the most likely explanation for MT and SQT flux enhancements that are not being reproduced by biogenic emission parameterizations.

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

~~measured values leading to an upper limit of daytime standardized sesquiterpene emission of $7.5 \cdot 10^{-3}$ nmol m^{-2} s^{-1} and $8.8 \cdot 10^{-3}$ nmol m^{-2} s^{-1} in 2015 and 2018, respectively.~~

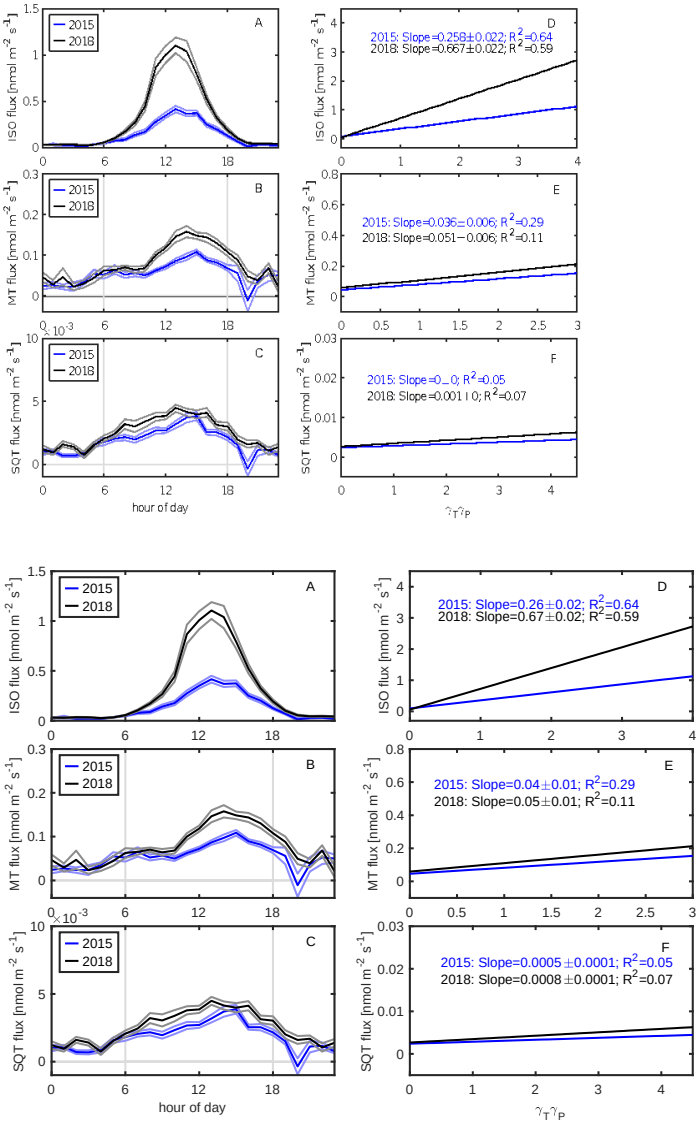
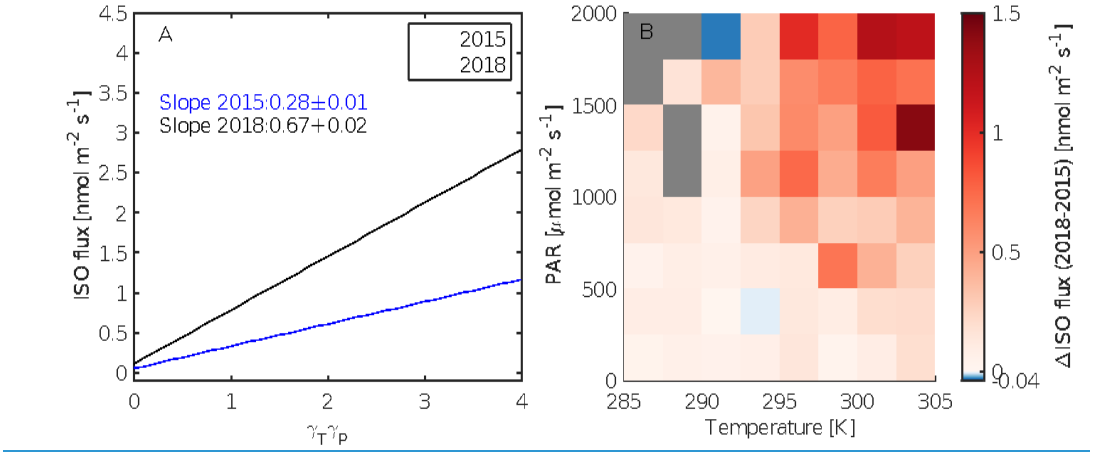


Figure 2: Diurnal cycles of average isoprene (A), monoterpene (B) and sesquiterpene (C) fluxes for the summers 2015 (blue) & 2018 (black), shaded areas indicate the standard error. Night-time fluxes are shown here for completeness of the diurnal cycle but gray shaded areas indicate that this data was not used for further analysis. **(D-F)** Daytime (6:00-18:00) isoprene, monoterpene, and sesquiterpene fluxes are plotted vs. theoretical temperature and light dependencies (Guenther et al. 2006, Guenther et al. 2012) including T24, T240, P24, P240. 2015 data are depicted in blue and 2018 data in black. The lines indicate a linear fit with fit parameters displayed within the plot. The slope of the fit parameter represents the standardized (303.15 K and 1000 PAR) emission factors. ~~show temperature binned isoprene, monoterpene and sesquiterpene fluxes respectively. The dashed lines depict~~

~~the theoretical temperature behavior based on Guenther et al. (1993) (G93) and Guenther et al. (1994) (G94) normalized to the respective fluxes at 303.15K.~~

3.3 Isoprene flux anomaly

The isoprene flux difference measured between the two summers of 2015 and 2018 is shown in Figure 2 A. Daytime maximum isoprene fluxes in 2018 were up to 2.7 times higher than in 2015. Isoprene fluxes are temperature dependent ~~Figure 2D represents the isoprene dependence on temperature.~~ (Guenther et al. 1993), light dependent (~~.~~ Monson and Fall, ~~(~~1989) as well as ~~found isoprene fluxes not only to depend on current temperature conditions, but also on current light conditions. In addition,~~ past 24h and 240h temperature and light conditions play a role (e.g. Guenther et al., 2006). These theoretical temperature and light parameters are plotted vs. the observed isoprene flux in Figure 2D based on the MEGAN big leaf approach (Guenther et al., 2006). Even after including both actual and past temperature and light parameters the difference in isoprene ~~emissions~~ fluxes between the two summers could not be resolved and standardized emission factors were still a factor 2.3 higher in 2018 than in 2015. Figure 3B shows that the difference was increasing with higher temperature and higher PAR values.



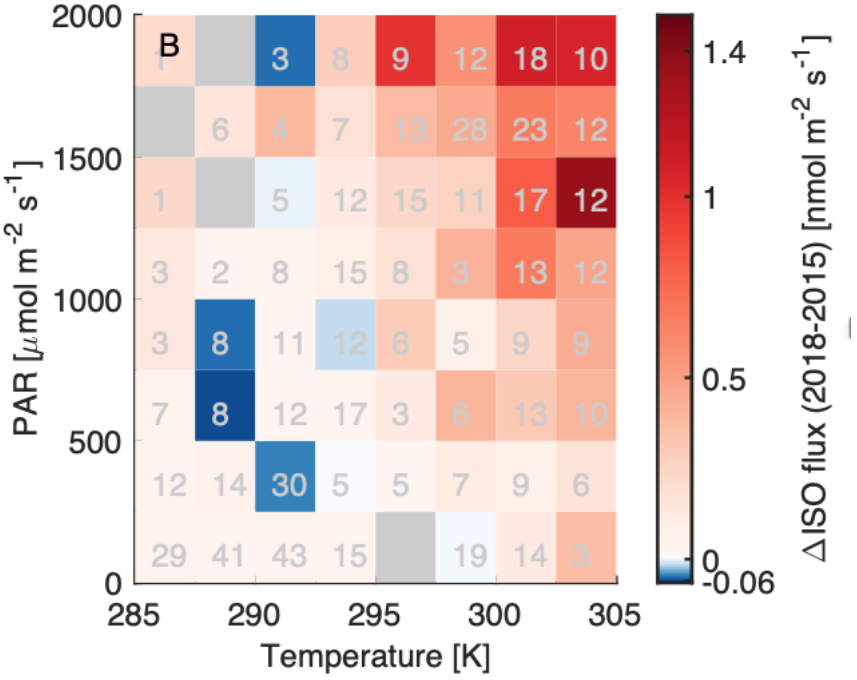


Figure 3: ~~A) Theoretical temperature and light dependencies (Guenther et al. 2006) including T24, T240, P24, P240 vs. observed isoprene flux in 2015 (blue) and 2018 (black). The lines indicate a linear fit with fit parameters displayed within the plot. The slope of the fit parameter represents the standardized (303.15 K and 1000 PAR) isoprene emission factors. B)~~ **Isoprene flux differences between 2018 and 2015 binned by temperature and PAR, positive differences are shown in red, negative in blue and bins with no available data are colored grey.** Grey numbers in the temperature/PAR fields indicate the number of observations for each temperature/PAR value pair.

In contrast to monoterpene and sesquiterpene ~~emissions~~fluxes, which exhibited comparable emission potentials between the two years and are mainly driven by evaporative emissions from storage

reservoirs (e.g. Kesselmeier and Staudt, 1999), it remains a puzzle why the isoprene emission potential was substantially higher in 2018 compared to 2015. As neither actual temperature and light dependencies nor 24h and 240h past temperature and light could explain the observed differences in isoprene fluxes, we investigated the following potential reasons: a) variation in the flux footprint, b) tree trimming, c) water availability/drought, and d) emission parameterization.

a) Figure 1 (left and middle panel) shows differences in the flux footprint densities between 2015 and 2018. ~~As shown in Figure 1A the footprint area in 2018 was smaller than the footprint in 2015.~~ Possible reasons for this are a change in flux tower position between the two years by ~50 m, as well as different meteorological conditions. In 2015, for westerly winds the flow regime may have been affected by the support structure and the building and consequently the analysis of isoprenoid fluxes was limited to the northeastern wind sector of [0°,120°]. Median daytime wind speed and direction in 2018 (affected by a heat wave) are similar to those in 2015 (Table S1). Median sonic temperature, sensible heat flux and friction velocity (see Table S1) were higher in 2018 resulting in stronger turbulent vertical transport with mostly friction velocity being responsible for the differences of the flux footprint density function between 2015 and 2018 (Fig 1). Multiplying the footprint density at each tree location with the basal emission factor of each tree species revealed a potential difference of 24% higher isoprene emissions in 2018 than in 2015. Even though the actual leaf area of each individual tree is not known and therefore neglected, this 24% of potential emission difference due to footprint density changes cannot explain the factor of 2.3 in observed ~~emissions~~ fluxes between the two years. Also growth of juvenile trees between the study years is unlikely to play a significant role, as just 8 % of the strong isoprene emitters were younger than 5 years in 2015. This analysis assumes that the trees from the tree inventory were responsible for the majority of measured isoprene ~~emissions~~ fluxes and that they were more important than emissions from short vegetation (e.g. lawn). Further supporting evidence that the flux footprint change cannot fully explain the observed differences derives from the fact that both monoterpenes and sesquiterpenes did not show significant inter-annual variations in their normalized emission potentials.

b) A second possible explanation for the isoprene flux difference could be ~~that trees underwent different trimming in the growing seasons which could lead to a~~ differen~~t~~ce~~s~~t in LAI in the two seasons, for example due to pruning, early leaf senescence or insect/pathogen damage. Personal communications from city gardeners revealed that of the trees most important for isoprene emissions in the study area (*Populus nigra*, *Populus alba*, *Quercus robur*) only poplar trees were cut differently in 2015 than in 2018. In 2015 only dead wood was removed from the poplars, whereas trees were cut more substantially in 2018. This would however lead to an expected smaller flux in 2018 than in 2015 due to reductions in leaf area. No observations on early leaf senescence or leaf damage by insects/pathogens were reported by the city gardeners during both study years.

c) A third possible explanation is that the growing season of 2018 was exceptionally dry with lower-than-average precipitation and large-sale, satellite-derived rootzone soil moisture (Figure 4A and 4B). Concurrent water flux observations, however, shown in Fig. 4C, indicate that on average the 2018 daytime summer water flux was 0.2 mmol m^{-2} s^{-1} higher than in 2015. Also the total surface water vapor conductance was 50 mmol m^{-2} s^{-1} higher in 2018 than in 2015. Higher

water fluxes observed in 2018 agree with anecdotal reports of city trees being artificially watered throughout the summer. Water fluxes in urban areas (maximum Bowen ratios observed in Innsbruck: 6 (Karl et al., 2020)) are generally very low (e.g. 5-6 times lower) when compared to measurements over purely vegetated surfaces, and therefore notoriously difficult to interpret. As such we cannot exclude the possibility of processes other than evapotranspiration from city trees contributing to higher water fluxes observed in 2018. An obvious explanation is that a significant water runoff during extensive watering operations resulted in increased evaporation over hot asphalt and other non-vegetated surfaces, leading to higher water fluxes in 2018. Water was also applied to asphalt surfaces more frequently during mornings to minimize the effect of urban aerosol pollution. The cumulative precipitation for July, August and September 2015 was 340 mm, and 258 mm for 2018. When taking just the campaign duration, the cumulative precipitation was 269 mm in 2015 and 136 mm in 2018. Since the 2018 campaign was shorter, we also calculated the cumulative precipitation for the same days as for the 2015 campaign. It was 203 mm in 2018. The precipitation data confirms an overall drier meteorological summer in 2018. It is well established that isoprene production in plants can decouple from photosynthesis during periods of drought and can be sustained by alternative metabolic carbon sources (e.g. Bertin & Staudt, 1996; Pegoraro et al., 2004a,b; Fortunati et al., 2008; Genard-Zielinski et al., 2014; Potosnak et al., 2014; Wu et al., 2015). The exact reason for biochemical regulation of isoprene emissions during drought is not fully unraveled, but has been suggested to represent a response for coping with heat stress (Loreto et al., 1998). Isoprene fluxes were observed to increase during the very early onset of drought conditions. For example, Seco et al. (2015) reported an increase in the ecosystem scale isoprene emission potential about one month before significant changes in pre-dawn leaf water potential were observed, but when CO_2 uptake was already decreasing. Additionally, they observed that the closing of stomata had a bigger effect on CO_2 than water fluxes, because gradual increases of vapor pressure deficit during the evening offset reduced leaf conductance. Isoprene is not controlled by stomata and would not be influenced by any changes in stomatal opening. In addition, their canopy scale observations suggested a shift of the temperature maximum of isoprene emissions towards higher temperatures from pre-drought to drought conditions. Otu-Larbi et al. (2019) reported a 2.5 fold increase in the isoprene emission potential during the same 2018 heat wave in a UK oak forest. They observed a strong temperature dependence of isoprene concentrations during the heat wave and discuss potential causes such as leaf temperature or rewetting enhanced emissions. While we do not have representative soil moisture data available for this study, we looked at precipitation data. Otu-Larbi et al. (2020) observed large increases in within- and above-canopy isoprene mole fractions in response to rainfall events after a 6-week drought in a temperate broadleaf forest, which they interpreted to result from enhanced isoprene emissions following the rewetting. We consider rewetting events an unlikely explanation for the observed higher isoprene fluxes in 2018 because, even though rainfall was reduced by half compared to 2015, rain-free time intervals were quite short (between 2 and 7 days) and thus no pronounced rewetting occurred after a long dry period. In fact, the isoprene flux time series suggests lower emissions following rain events.

We would like to note that both mono- and sesquiterpene emissions are also controlled by

stomatal conductance which could be expected to affect emission rates during drought periods (see e.g. Niinemets and Reichstein, 2003a & b). We did not observe significant differences of mono- and sesquiterpene fluxes between the seasons.

d) We also examined the impact of emission model framework on isoprene emissions. Due to the lack of directly measured soil moisture ~~water content~~ data, which would be hard to interpret in an urban context, the drought effect was not included in the emission model parameterization. Precipitation (Fig. 4A) and large-scale satellite-derived soil moisture data (Fig. 4B) suggest 2018 being drier than 2015, corresponding to a significant heat wave in the summer of 2018. Severe drought conditions would reduce isoprene emissions further and therefore could not explain an increased isoprene emission potential in 2018. The fact that evaporative water fluxes however were comparable between 2015 and 2018 (and if at all were somewhat higher in 2018), suggest that the trees might not have undergone a severe drought episode in both years. Mild drought has been observed to lead to increases of isoprene emissions (e.g. Otu-Larbi et al., 2019). To investigate relative changes between emission model frameworks we also set up a MEGAN 5-layer canopy model (Guenther et al., 2006) for different scenarios. We recognize that the concept of an LAI for the 5 layer model is based on the assumption of a homogeneous vegetation distribution. The resulting fraction of sun vs shade leaves for urban vegetation might therefore not be fully constrained without complex 3D radiative transfer simulations in urban situations with sparsely distributed vegetation. The prescribed setup however was chosen to mimic a high sunlight fraction of the biomass with an overall fraction of 64%. The model setup was in turn only used to see whether differences between 2015 and 2018 could theoretically be explained by a high sunlight fraction or different temperature response curves. We observed that a shift in T_{opt} towards higher temperatures helped minimize the observed difference between the two years (e.g. 10% to 40%) best. So, for example T_{opt} set to 313 K could explain about half of the flux enhancement. This would leave predicted isoprene emission fluxes underestimated by about 50% in 2018.

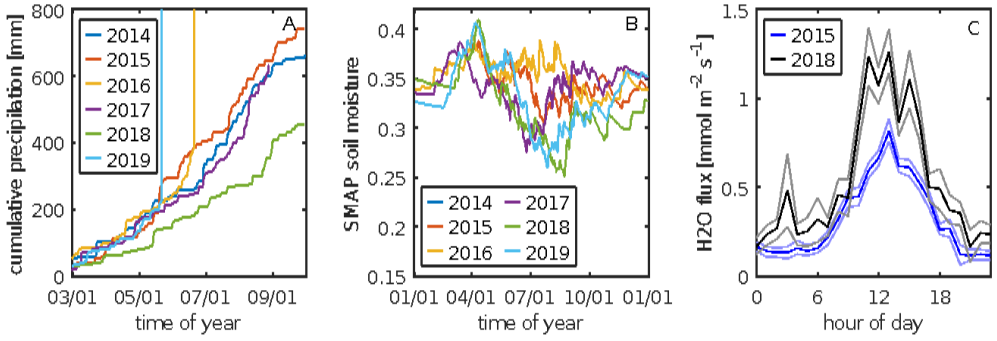


Figure 4: A) cumulative precipitation for the growing seasons of 2014-2019 B) annual SMAP satellite soil moisture of the rootzone from 2014-2019. C) diurnal cycle of water fluxes measured in 2015 (blue) and 2018 (black).

3.4 Top-down flux and bottom-up ~~BVOC~~ isoprenoid ~~flux~~ emission ratios

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

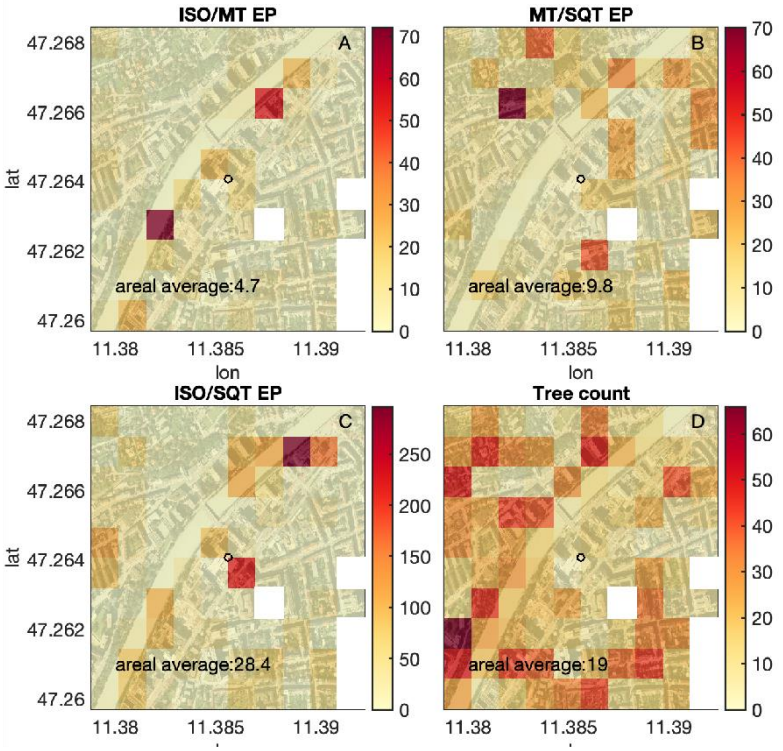


Figure 5: A-C: Bottom-up estimates of standardized ISO/MT, MT/SQT and ISO/SQT emission ratios based on literature values (see Table 1). D: Tree count. Maps were created in Matlab (www.mathworks.com) and are based on OpenStreetMap (https://www.openstreetmap.org/copyright) under the CC BY 3.0 AT license.

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. Assuming the same correlation between isoprene and benzene fluxes in early spring before the start of the vegetation period and the summer months results 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) has previously revealed two biogenic factors: one light- and temperature-dependent for isoprene and a second mostly temperature-dependent including monoterpenes and sesquiterpenes. 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. Interannual comparison of biogenic fluxes revealed up to three times higher isoprene fluxes in 2018, when a heat wave persisted, than in 2015. Monoterpene fluxes were an order of magnitude lower than isoprene fluxes and sesquiterpene fluxes were another order of magnitude lower than monoterpene fluxes, however both summer fluxes were comparable for these two terpenoid classes after standardization. Our findings show a higher interannual variability of

isoprene emissions compared to monoterpenes and sesquiterpenes. Normalizing isoprene fluxes to standard light conditions did not fully remove the interannual difference, but decreased the factor from 3 to 2.3. The difference increased with higher temperature and higher PAR values. Analysis of footprint, precipitation and a coarse-scale satellite-based soil moisture product as a proxy for plant water availability, and pruning activity differences of the two summers did not completely 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 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, Otu-Larbi et al., 2019). 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. Here a change of T_{opt} towards a higher temperature optimum could explain another 50% of the observed isoprene emission flux difference between 2015 and 2018. In conjunction with changes in flux footprints (24%) these two effects could account for about ~75% of the difference. If generalized, our observations suggest distinct differences that urban trees experience, possibly due to significantly altered environmental conditions (e.g. stresses, light and temperature environment). 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.

~~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~~ssuming the same ~~correlation between isoprene and benzene fluxes in early spring before the start of the vegetation period can be extrapolated to~~and ~~the summer months~~ results in~~. 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 three times higher isoprene fluxes in 2018, when a heat wave persisted, than in 2015. Monoterpene emissions fluxes were an order of magnitude lower than isoprene emissions fluxes and sesquiterpene emissions fluxes were another order of magnitude lower than monoterpene emissionsfluxes, however both summer emissions fluxes 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 2.3. The difference increased with higher temperature and higher PAR values. Analysis of footprint, precipitation and a coarse-scale satellite-based soil moisture product as a proxy for plant 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 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, Otu-Larbi et al., 2019). 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.

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Innsbruck. The City of Innsbruck is acknowledged for making the city tree inventory available, Michael Steiner for complementing it with trees in private spaces.

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.

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 km^2 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 carnea	8	0.00[g)]	12.00[g)]	0.025[*)]
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)]