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Interannual variability of terpenoid emissions in an alpine city

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Supplemental Information:

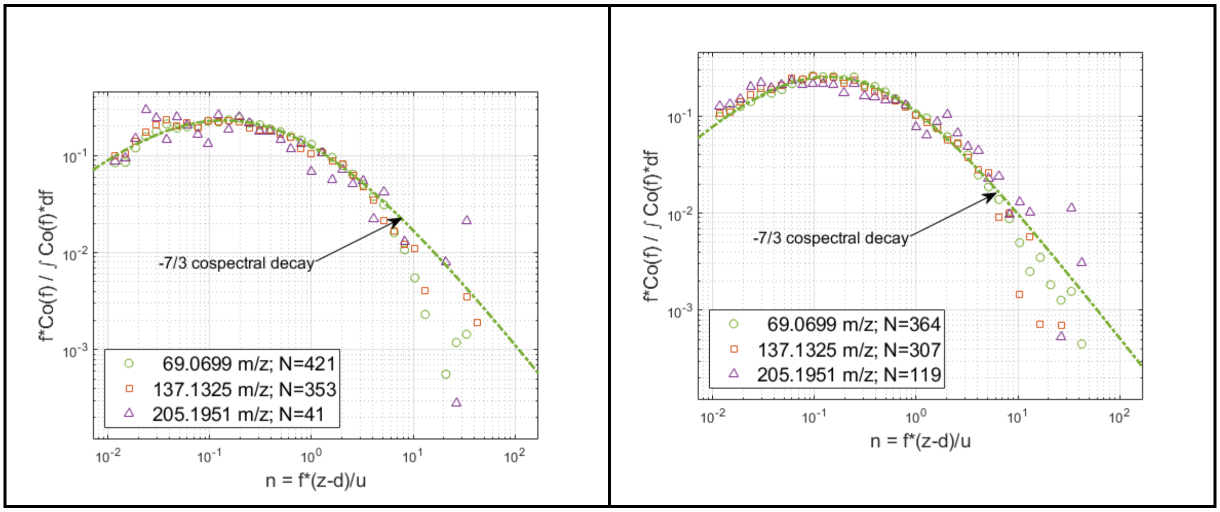

Figure S1: Average normalized co-spectra of isoprenoids signals with vertical wind speed for the data records of 2015 (left panel) and 2018 (right panel). The mass channels 69.0699 m/z, 137.1325 m/z, and 205.1951 m/z correspond to the protonated ions of isoprene, sum of monoterpenes and sum of sesquiterpenes, respectively.

Selection of contributing half-hours according to wind sector [0°,120°] and daytime (06:00 – 18:00). Following Foken (2017) guideline for spectral analysis QA/QC filter criterion is applied at quality level 3. In addition, data were also filtered for flux signal-to-noise ratio (SNR > 3), and for u* > 0.15. Due to the normalization of the co-spectra by the flux magnitude individual half-hour spectra corresponding to fluxes close to zero cause numerical problems (not shown) which were avoided by omitting half-hours where the absolute value of the flux magnitude falls below 0.005 nmol m^{-2} s^{-1}. The number of half-hours passing all filters and thus contributing to the respective average co-spectrum is indicated by N in the legends.

The green lines are least square fits of an analytical model co-spectrum (see Eq 4.2 in Lee et al. (2004)) to the respective isoprene co-spectra with unity fit weights in the band of 1.5 decades around the frequency of the co-spectral maximum steeply tapering off to zero outside that band. Transfer functions for sensor separation, path averaging of the sonic anemometer and of the PTR drift tube, and tube attenuation of the turbulently purged inlet system (high flow sampling transfer line [sonic sampling manifold in lab] as well as sub-sampling capillary [manifold PTR-Qi-TOF VOC analyzer] are used for the description of the high frequency loss of the inlet system. The product of the model co-spectrum with these transfer functions represents the lowpass filtered co-spectrum; ratios of the integrals of filtered over unfiltered co-spectral densities describe high frequency attenuation of the VOC sampling system. Slopes of the linear regression of filtered versus unfiltered covariances estimate the average attenuation of isoprene, monoterpene, and sesquiterpene fluxes to be 4% or less.

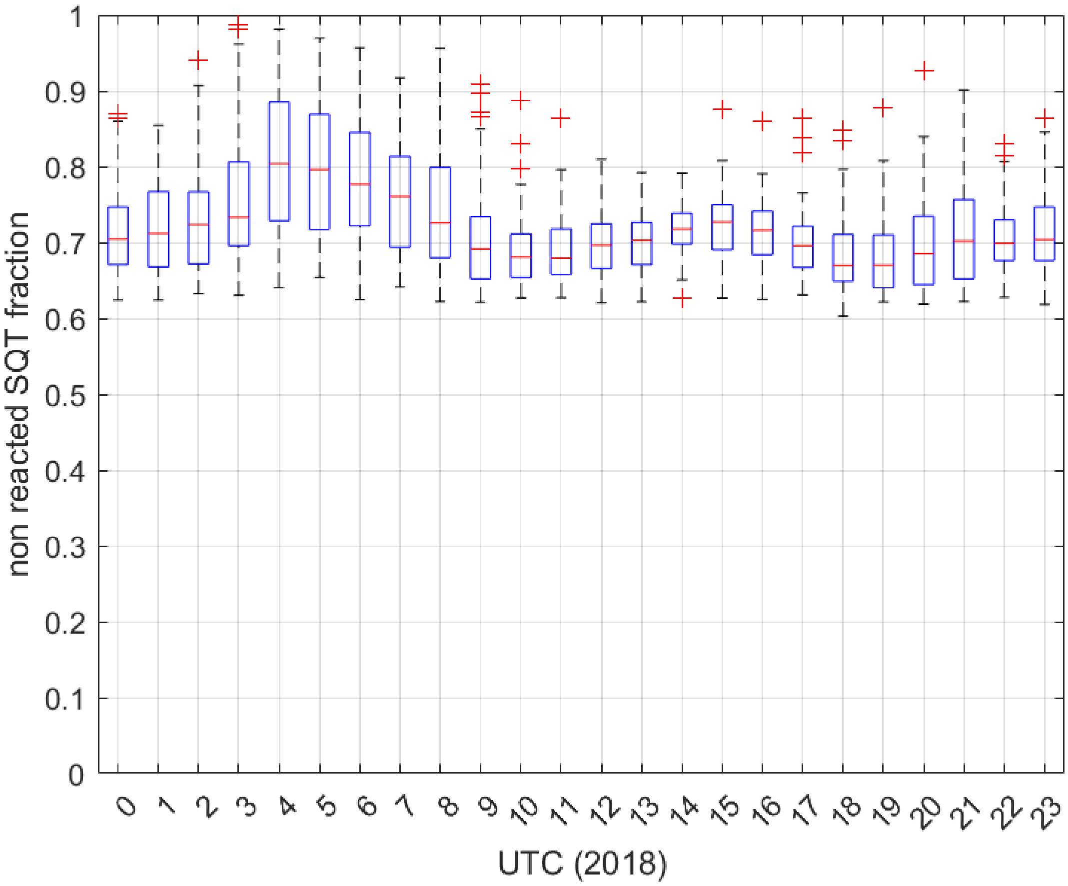

Figure S2 Non reacted total sesquiterpene flux due to reaction with ozone assuming a mixture of 36 % rSQT and 64% nrSQT

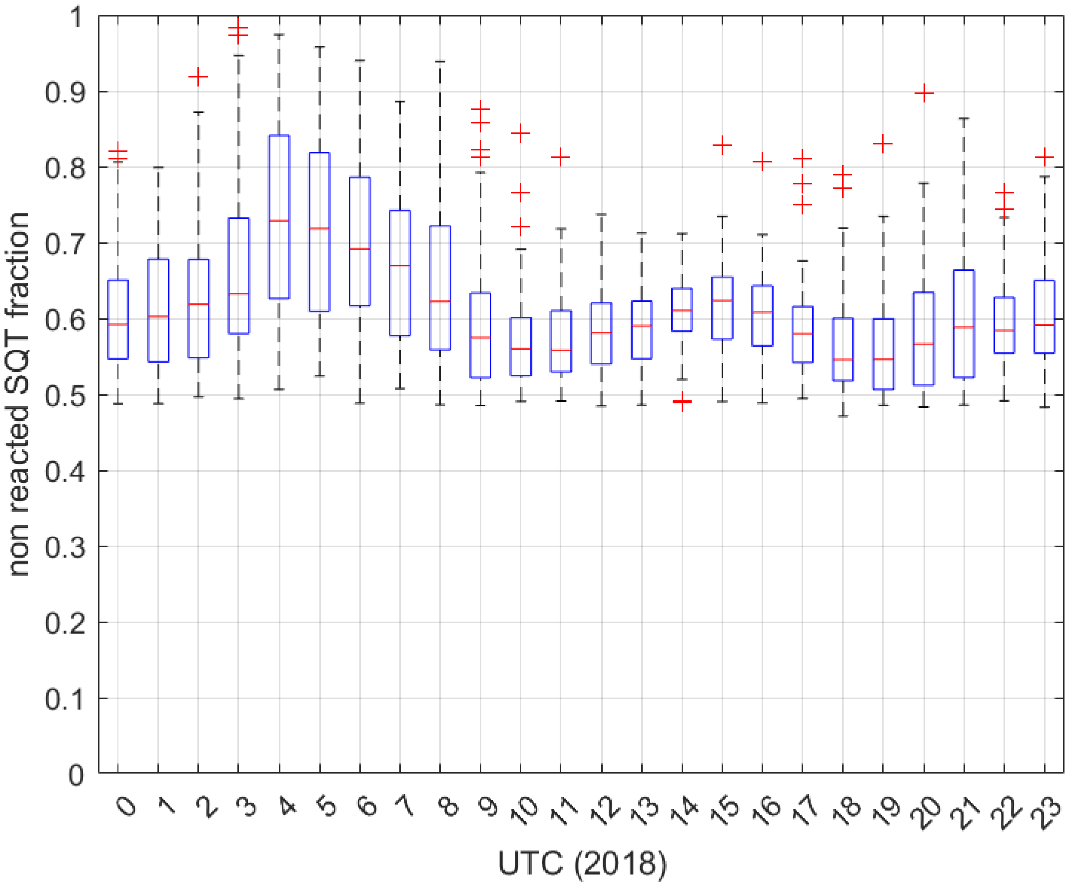

Figure S3 Non reacted total sesquiterpene flux due to reaction with ozone assuming a mixture of 50 % rSQT and 50% nrSQT

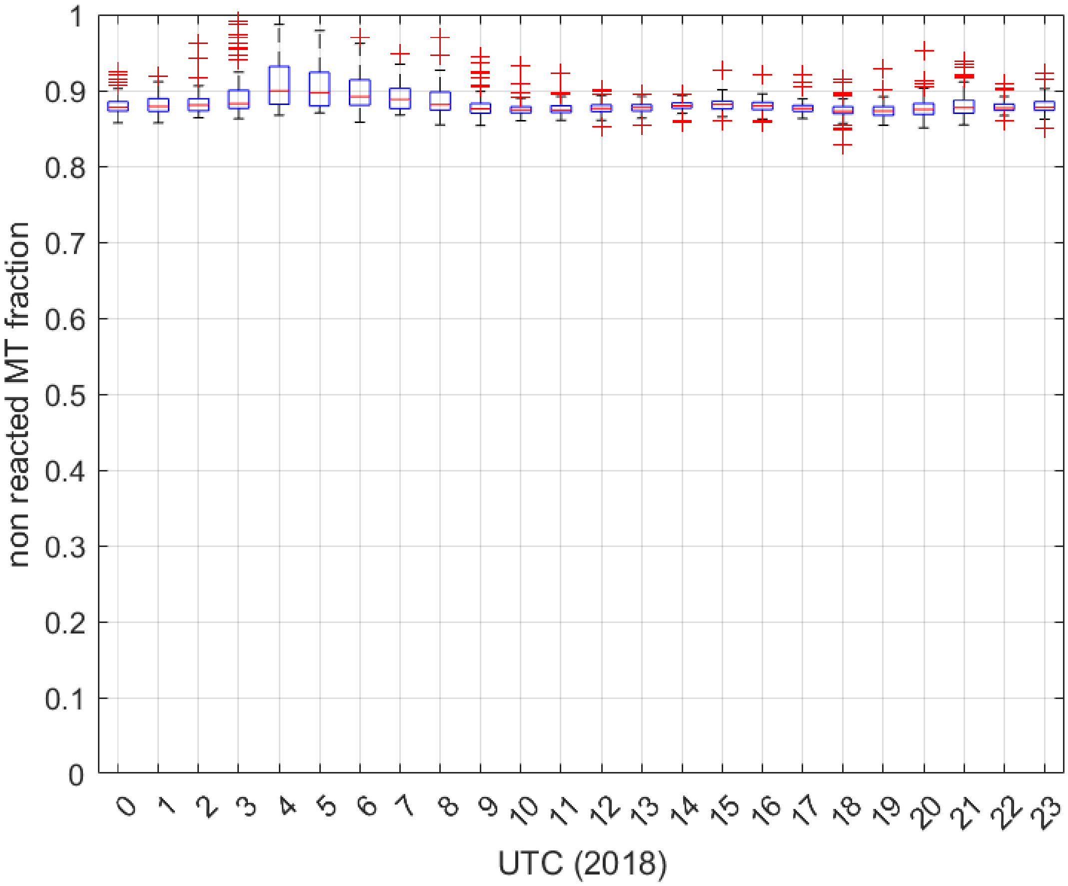

Figure S4 Non reacted total monoterpene flux due to reaction with ozone assuming 12% ocimene .

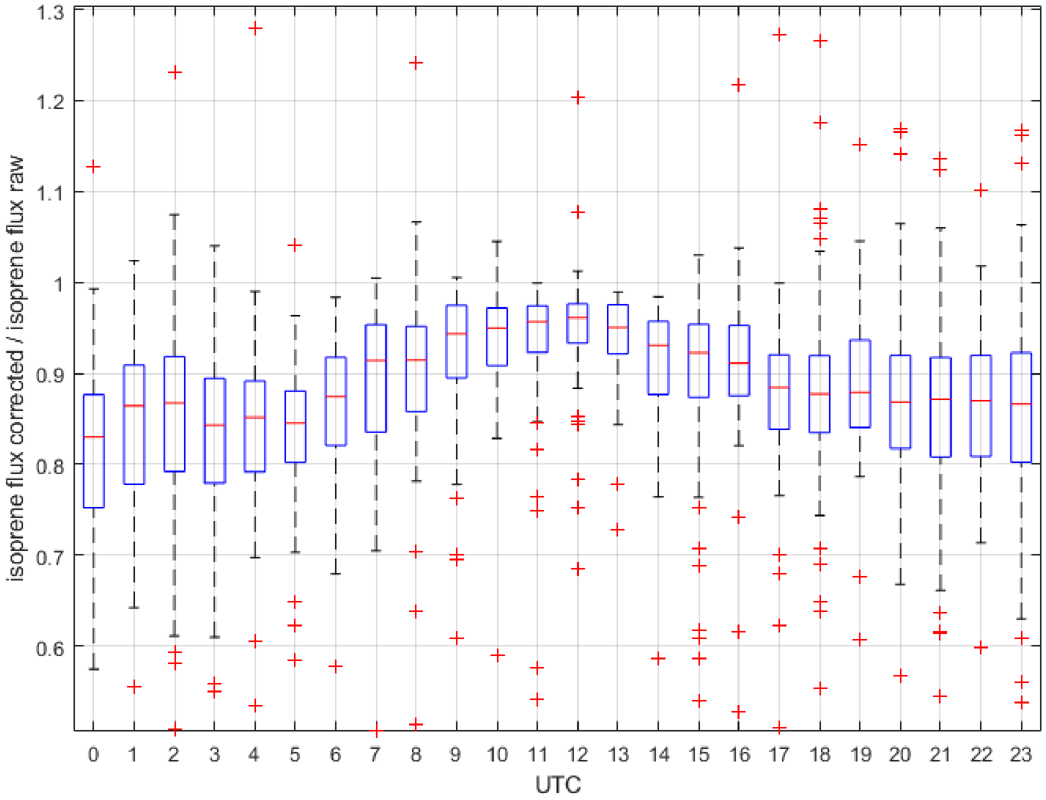

Figure S5: Modelled contribution of traffic related isoprene emissions using the COPERT (https://www.emisia.com/utilities/copert/) traffic emission model and data from Reimann et al., (2000)

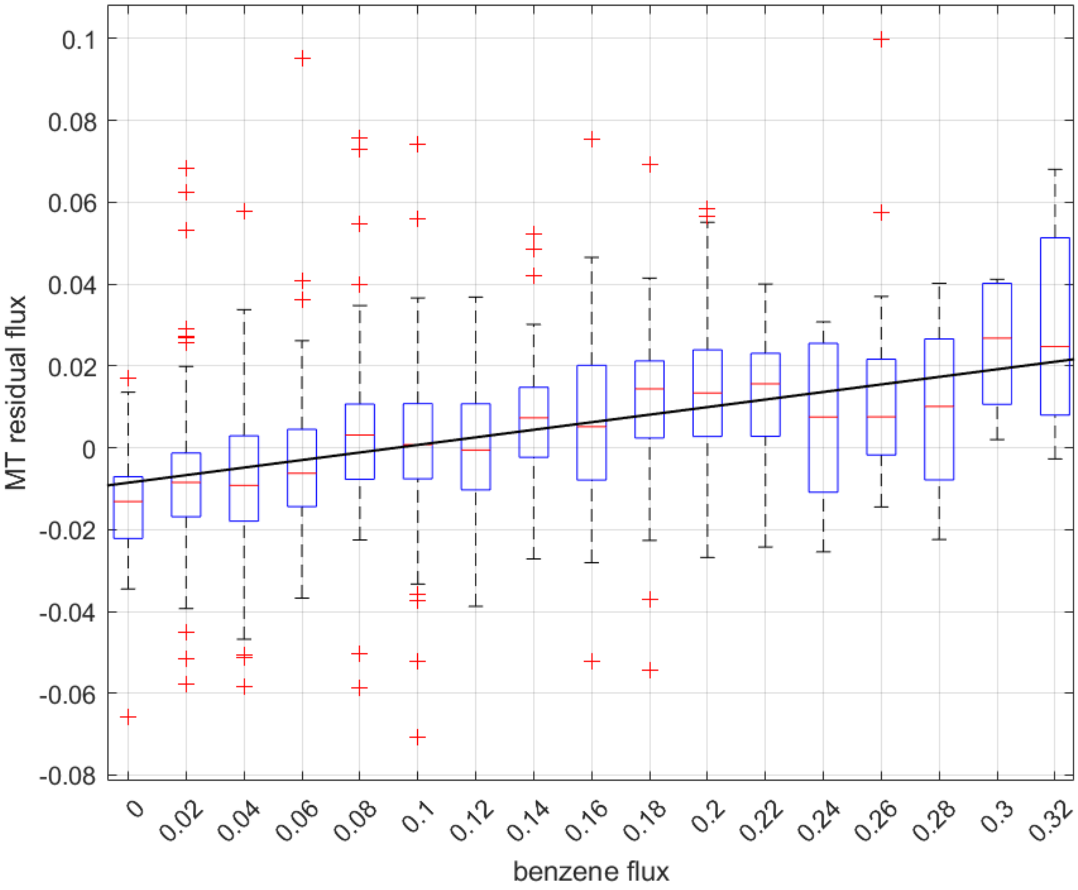

Figure S6: Residual of the observed vs fitted monoterpene flux plotted versus benzene flux. The residual was calculated using the biogenic emission parameterization fit from Fig. 2 (flux units are nmol/m2/s)

Table S1: Comparison of meteorological and turbulence parameters. Statistics were limited to [1] summer (July, August, September), [2] July 27 - Sept 2, [3] the respective eddy covariance dataset restricted to daytime (6-18h local time) and northeastern wind sector [0°,120°] and QA/QC levels of 6 or less according to Foken, 2017 (see main text for details).

	remark	2015	2018
sum of precipitation	**[1]**	**340.0 mm**	**258.1 mm**
sum of precipitation	**[2]**	**158.5 mm**	**155.4 mm** **(57 mm between Aug 29-31)**
sunshine duration	**[1]**	**690.2 h**	**719.0 h**
sunshine duration	**[2]**	**294.2 h**	**302.5 h**
Median sonic temperature (T)	**[3]**	**294.1 K**	**299.2 K**
Median sensible heat flux ()	**[3]**	**0.05 K m s-1**	**0.11 K m s-1**
Median friction velocity (*)	**[3]**	**0.30 m s-1**	**0.41 m s-1**
Median Obukhov length (L)	**[3]**	**-42.0 m**	**-58.8 m**
Median wind speed (U)	**[3]**	**2.27 m s-1**	**2.44 m s-1**

Summer 2018 saw over 80 mm less rain than summer 2015. Precipitation during the experimental period of 2018 is comparable to the same period of 2015, however, in 2018 57 mm of rain fell only between Aug 29-31 at the end of the campaign.

Sunshine duration of the summer periods as well as the period of Jul 27 - Sep 2 were similar.

The measurement period in 2018 (affected by a heat wave) saw significantly higher median sensible heat flux, $\underline{w'T'}$, (i.e. more convective situation) and significantly higher median friction velocity, u_*, compared to 2015. Difference of Obukhov length, $L = -\frac{u_*^3}{\kappa \cdot \frac{g}{T} \cdot \underline{w'T'}}$, where κ is the von Carman constant, and g is the gravitational acceleration, are a consequence of differences in u_*, $\underline{w'T'}$, and T. Both higher u_* and more convection in 2018 enhance the turbulent vertical transport and consequently the flux footprint density function tends to be less stretched out compared to 2015 (see Figure 1). Testing the FFP model (Kljun et al. 2015) for its sensitivities to the input parameters it turns out that u_* strongly affects the flux footprint density function whereas L has very little influence in the parameter sub-domain relevant for the summer studies.

Supplemental References:

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