



Supplement of

Measurements of atmospheric C₁₀–C₁₅ biogenic volatile organic compounds (BVOCs) with sorbent tubes

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Table S1. List of sorbent tubes used (SS=stainless steel, Silco= SilcoNert 1000) in different experiments

Adsorbent tubes (number of tubes used)	Brand	Tube material	Packing	Dimensions	Experiments
Tenax TA 60/80 (15)	Supelco	SS	Commercial	3.5" x 1/4"	Storage stability, breakthrough, sampling efficiency, intercomparison
Tenax TA 60/80 (15)	Supelco	SS	Self-packed	3.5" x 1/4"	Storage stability, breakthrough, sampling efficiency, tube material
Tenax TA 60/80 (9)	Markes	Silco	Self-packed	3.5" x 1/4"	Storage stability, sampling efficiency, tube material
Carbopack B (15)	Supelco	SS	Commercial	3.5" x 1/4"	Storage stability, breakthrough, sampling efficiency, intercomparison

S1. Generation of gas mixtures using ReGaS2 generator

5 The gas mixture generation using ReGaS2 (Pascale et al., 2017) was based on the permeation method, which is a dynamic volumetric method described in the international standard ISO 6145-10. Permeation tubes containing the compounds under study – α -pinene (Fine Metrology, Italy; assessed purity = 92.0 %) and β -pinene (VICI Metronics, WA, USA; assessed purity = 88.9 %) – were calibrated using METAS magnetic suspension balance (Macé et al., 2022) prior the generation. The calibration temperature range for α -pinene was 40 – 45 °C and 35 – 40 °C for β -pinene. Within this range, three permeation rates for each compound were estimated to obtain the calibration curve (exponential relationship between permeation rate and temperature) required by ReGaS2 software.

S1.1 Set-up for the evaluation tests of sorbent tubes

15 ReGaS2 generator was used to produce stable amount fractions (~ 10 nmol mol⁻¹) of α -pinene and β -pinene in zero air, which was produced by a zero air generator (HPZA-7000, Parker Balston, Lancaster, NY, USA). The calibrated permeation units provided by METAS were placed in the ReGaS2 oven. Before starting the generation, ReGaS2 was left for two days in transport mode for stabilization. To generate terpene rich air, the dilution flow of ReGaS2 was set at 5.94 L min⁻¹. The amount fractions of terpenes generated by ReGaS2 were still too high for the tests, therefore, the air was further diluted by humidified air produced by bubbling the zero air through the ultrapure water (Milli-Q Gradient, Molsheim, France).

S1.2 Set-up for the interlaboratory comparison

IMT Nord Europe used ReGaS2 to produce terpene rich air (α -pinene, β -pinene), which was loaded into the sorbent tubes used in the interlaboratory comparison (Fig. S1). The matrix gas was nitrogen (MESSER FRANCE SA, purity 99.999 %). The calibrated permeation tubes provided by METAS (α -pinene, β -pinene and, additionally, toluene as internal reference), were placed in the ReGaS2 oven. Before starting the generation, ReGaS2 was left one day in transport mode ($T_{\text{oven}}=42$ °C, carrier flow = 0.5 L min⁻¹, dilution flow = 0.5 L min⁻¹, pressure=1.08 bar). During the generation, the carrier flow was set at 1.0 L min⁻¹. The output flow was set at 1 L min⁻¹ and externally diluted with a flow of 5.09 L min⁻¹ of humid nitrogen (55–60 % relative humidity). One hour after starting the generation mode, the sorbent tube loading took place. Four sorbent tubes in parallel (Fig. S3) were loaded using 50 mL min⁻¹ for a duration of 15 min for half of the total tubes and 30 min for the rest half of the total tubes. In total, 16 Tenax TA and 16 Carbopack B sorbent tubes were loaded.

S2. Calculation of uncertainties

The relative combined uncertainty of the terpene amount fraction ($u(C_i)$) measured in the tubes was estimated by considering the relative standard uncertainties of the loaded mass (m_i , ng) and of the sampling volume (V , L) (Eq. S1):

$$\frac{u^2(C_i)}{C_i^2} = \frac{u^2(m_{i,meas})}{m_{i,meas}^2} + \frac{u^2(V)}{V^2} \quad (\text{S1})$$

The uncertainties on the mass calculations can be described as the result of the propagation of the uncertainties on several parameters. The first parameter is linked to the integration of the peaks in the chromatogram, a second one is linked to the calibration standard uncertainty ($u(m_{\text{calibration}})$), a third one is linked to the repeatability ($u(X_{i,\text{repeatability}})$) of the calibration standard and a fourth one is linked to the blanks of the tubes. Considering that the integration of the chromatograms was very good the total uncertainty of the loaded mass can be calculated by Eq. (S2):

$$\frac{u^2(m_{i,meas})}{m_{i,meas}^2} = \frac{u^2(m_{i,\text{calibration}})}{m_{i,\text{calibration}}^2} + \frac{u^2(X_{i,\text{repeatability}})}{X_{i,\text{repeatability}}^2} + \frac{u^2(X_{i,\text{blank}})}{X_{i,\text{blank}}^2} \quad (\text{S2})$$

The sampling volume was calculated as the product of the flow (q_v , L min⁻¹) passing through the tube by the loading time (t , min) (Eq. S3):

$$V = q_v \cdot t \quad (\text{S3})$$

Thus, the relative combined uncertainty of the sampling volume ($u(V)$) was calculated as the propagation of the respective standard uncertainties of flow and time (Eq. S4):

$$\frac{u^2(V)}{V^2} = \frac{u^2(q_v)}{q_v^2} + \frac{u^2(t)}{t^2} \quad (\text{S4})$$

Where the uncertainty on the flow is: $u(q_v) = \frac{\pm 3 \% \cdot q_v}{\sqrt{3}}$.

The standard uncertainty of the sampling times used – 15 min and 30 min – was assumed to follow a rectangular distribution. The estimated values of uncertainty were the following:

$$u(t_{15}) = \frac{10}{\sqrt{3}}; \quad u(t_{30}) = \frac{20}{\sqrt{3}}$$

S2.1 FMI uncertainty

Here detailed description on the uncertainty calculation for the for α -pinene, β -pinene and toluene is given as an example. Table 1 in main manuscript presents the total uncertainties of all studied compounds.

The calibration uncertainties at FMI are: $\frac{u^2(m_{i,calibration})}{m_{i,calibration}^2} = 2 \%$ for all compounds and $\frac{u^2(X_{i,repeatability})}{X_{i,repeatability}^2} = 2 \%$ for all compounds in Tenax TA and 4 %, 12 % and 2 % for α -pinene, β -pinene and toluene in Carbopack B tubes, respectively. $\frac{u^2(X_{i,blank})}{X_{i,blank}^2} = 0.15\text{--}0.6 \%$ for toluene in Tenax TA and Carbopack B tubes. For α - and β -pinene no blank was observed. The individual relative expanded uncertainty of each measurement is 6.8 – 24.6 % (coverage factor (k)=2) for all the tubes, whereas the averaged expanded uncertainty of the amount fractions for each set of 4 tubes in laboratory intercomparison experiments was 3.4–12.3 % (k=2, Eq. S5).

$$\frac{u_{C_i,avg}}{C_{i,avg}} = \frac{1}{n} \sqrt{\sum_{i=1}^n u_{C_i}^2} \quad (\text{Eq. S5})$$

More details for each uncertainty source and for the two types of sorbent material are indicated in Table S2.

S2.2 IMT Nord Europe uncertainty

The calibration uncertainties at IMT Nord Europe are: $\frac{u^2(m_{i,calibration})}{m_{i,calibration}^2} = 2.0 \%$, 1.5 % and 1.3 % for α -pinene, β -pinene and toluene respectively and $\frac{u^2(X_{i,repeatability})}{X_{i,repeatability}^2} = 2 \%$ for all compounds (k=1). The individual relative expanded uncertainty of each measurement is 6.0 % and 6.8 % (k=2) for all the tubes, whereas the averaged expanded uncertainty of the amount fractions for each set of 4 tubes was 3.0–3.4 % (k=2, Eq. S5).

More details for each uncertainty source and for the two types of sorbent material are indicated in Table S3.

Table S2. Sources of individual uncertainty (k=1) and averaged uncertainty for intercomparison tests (k=1) for Tenax TA (n=4) and Carpack B tubes (n=4) at FMI.

Compound	$\frac{u(V)}{V}$ (%)	$\frac{u(m_{i,calibration})}{m_{i,calibration}}$ (%)	$\frac{u(X_{i,repeatability})}{X_{i,repeatability}}$ (%)	$\frac{u(X_{i,blank})}{X_{i,blank}}$ (%)	$\frac{u_{C_i}}{C_i}$ (%)	$\frac{u_{C_i,avg}}{C_{i,avg}}$ (%)
Tenax®TA						
α-pinene	1.8	2.0	2.0	negligible	3.4	1.7
β-pinene				negligible	3.4	1.7
Toluene				0.15	3.4	1.7
Carpack B						
α-pinene	1.8	2.0	4.0	negligible	4.8	2.4
β-pinene			12.0	negligible	12.3	6.1
Toluene			2.0	0.6	3.4	1.7

Table S3. Sources of individual uncertainty (k=1) and averaged uncertainty for intercomparison tests (k=1) for Tenax TA (n=4) and Carbopack B tubes (n=4) at IMT Nord Europe.

Compound	$\frac{u(V)}{V}$ (%)	$\frac{u(m_{i,calibration})}{m_{i,calibration}}$ (%)	$\frac{u(X_{i,repeatability})}{X_{i,repeatability}}$ (%)	$\frac{u(X_{i,blank})}{X_{i,blank}}$ (%)	$\frac{u_{C_i}}{C_i}$ (%)	$\frac{u_{C_i,avg}}{C_{i,avg}}$ (%)
Tenax®TA						
α-pinene	1.8	2.0	2.0	negligible	3.4	1.7
β-pinene		1.5		negligible	3.1	1.6
Toluene		1.3		0.4	3.0	1.5
Carbopack B						
α-pinene	1.8	2.0	2.0	negligible	3.4	1.7
β-pinene		1.5		negligible	3.1	1.6
Toluene		1.3		0.7	3.1	1.6

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55 **Supplement figures:**

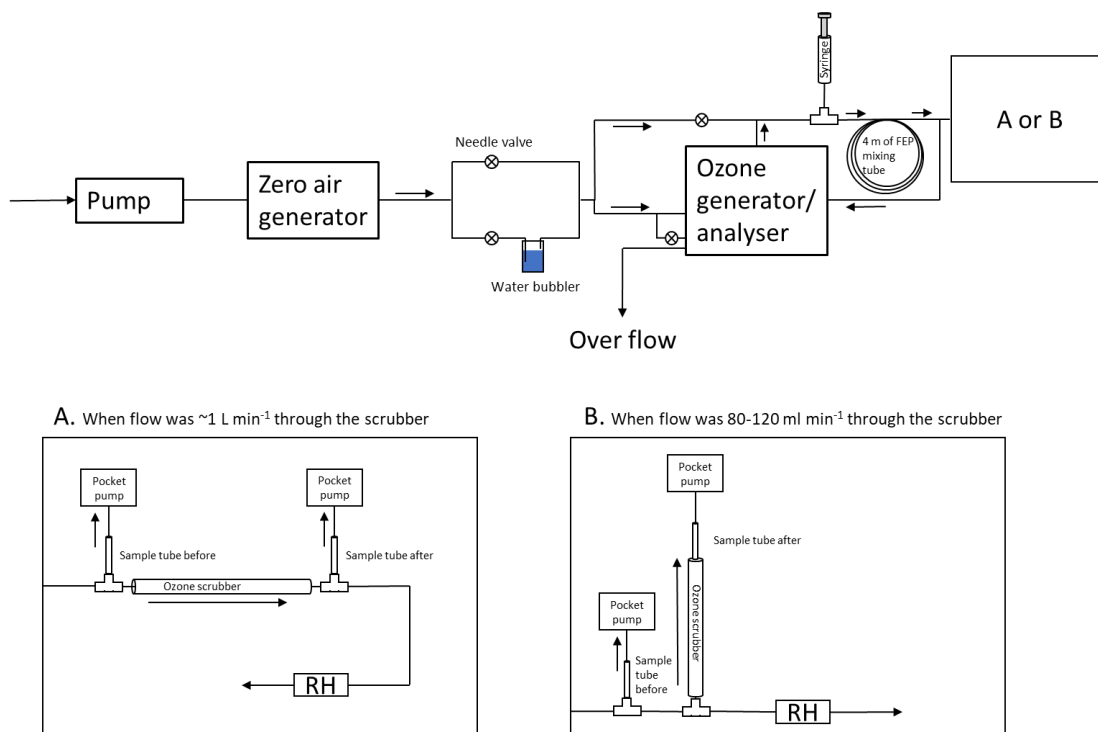


Figure S1. Schematic of the setup for O₃ scrubber measurements

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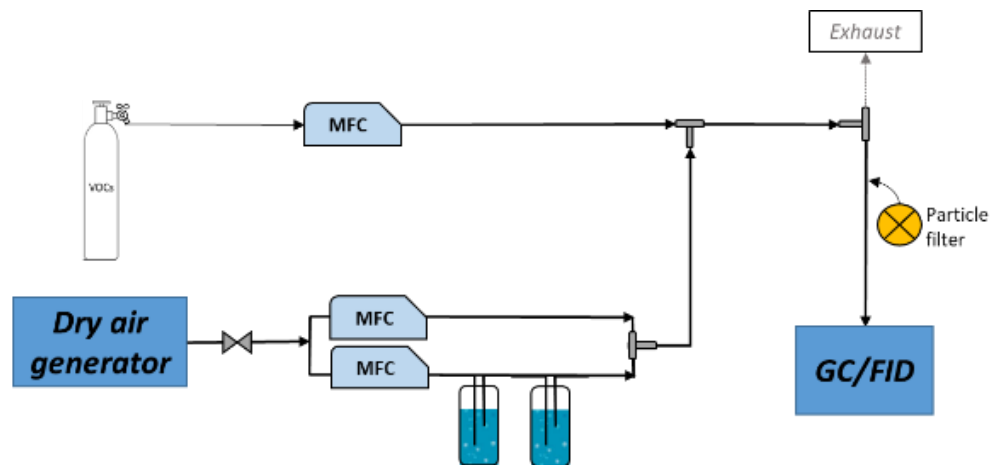


Figure S2. Schematic of the setup for test of particle filters at IMTelecom for terpenes.

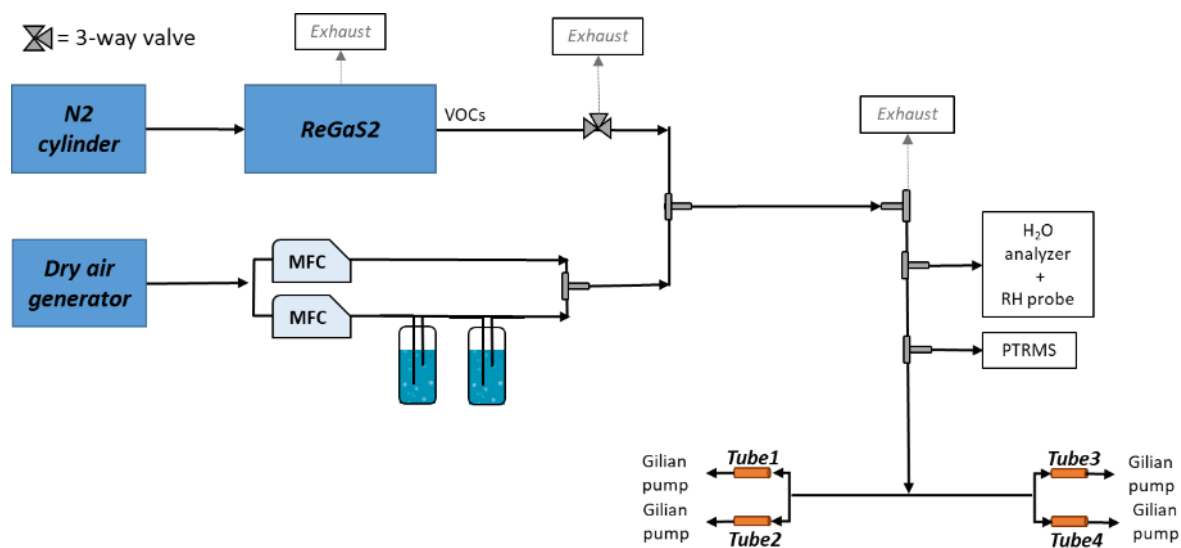
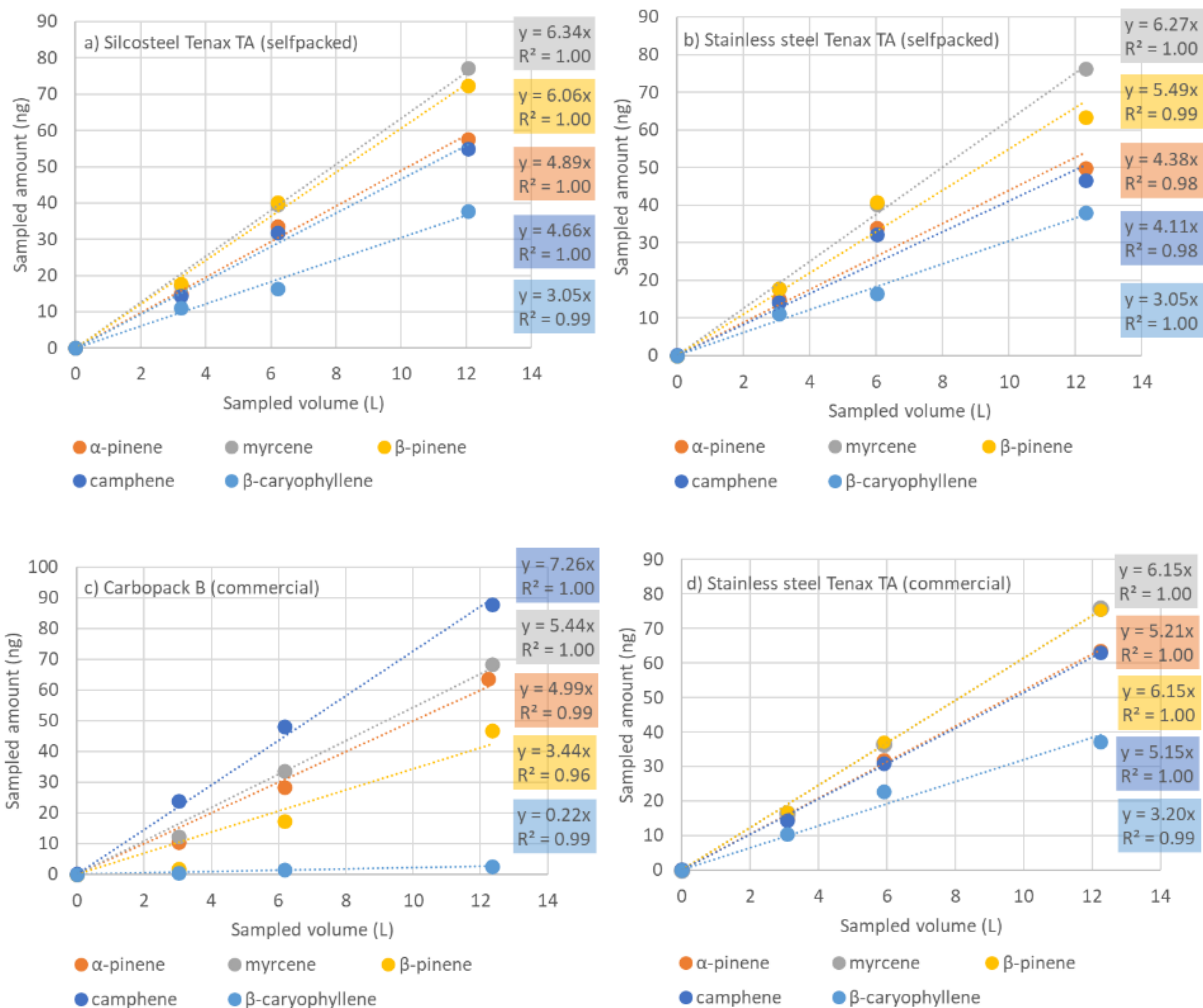


Figure S31. Schematic of set-up for sorbent tubes loading during intercomparison experiment.



70 **Figure S4.** Linearity of terpenes sampled with a) SilcoNert 1000 Tenax TA (self-packed), b) stainless steel Tenax TA (self-packed), c) Carbopack B (commercial) and d) stainless steel Tenax TA (commercial) sorbent tubes at RH ~70%. Since we did not find any blank for these compounds in the used sorbent tubes, zero was used as one point.

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