1 The importance of cylinder passivation for preparation and long-term stability of 2 multicomponent monoterpene primary reference materials

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1314 Abstract

Monoterpenes play an important role in atmospheric chemistry due to their large anthropogenic 15 and biogenic emission sources and high chemical reactivity. As a consequence, measurements 16 are required to assess how changes in emissions of monoterpenes impact air quality. Accurate 17 and comparable measurements of monoterpenes in indoor and outdoor environments require 18 gaseous primary reference materials (PRMs) that are traceable to the international system of 19 units (SI). PRMs of monoterpenes are challenging to produce due to the high chemical 20 21 reactivity and low vapour pressures of monoterpenes and also their propensity to convert into other compounds, including other terpenes. In this paper, the long-term stability of 22 23 gravimetrically prepared static monoterpene PRMs produced in differently passivated cylinders, including sampling canisters, was assessed. We demonstrate that static PRMs of 24 multiple monoterpenes can be prepared and used as a suitable long-term standard. For the first 25 26 time the effect of cylinder pressure and decanting from one cylinder to another on the chemical composition and amount fraction of monoterpenes was also studied. Gravimetrically prepared 27 PRMs of limonene in high pressure cylinders were compared to a novel portable dynamic 28 reference gas generator based on dilution of pure limonene vapour emitted from a permeation 29 30 tube. 31

- 32 Keywords
- 33 Monoterpenes, gravimetrically prepared standards, long-term stability, cylinder passivation,
- 34 sampling vessels, dynamic standard system, permeation, primary reference material
- 35

3637 1. Introduction

Terpenes are a large and diverse family of naturally occurring organic compounds that are a major biosynthetic building block (de Meijere et al., 1998; Nicklaus et al., 2013). Vegetation including forests and agricultural crops (Curtis et al., 2014; Ormeño et al., 2010) emit substantial quantities of isoprene (a hemiterpene (C_5H_8)), monoterpenes ($C_{10}H_{16}$) and sesquiterpenes ($C_{15}H_{24}$) (Barkley et al., 2008; Jokinen et al., 2015; Smolander et al., 2014; Squire et al., 2014; Tao and Jain, 2005).

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Terpenes play an important role in atmospheric chemistry due to their high reactivity influencing the HO_x and NO_x budgets (Carslaw et al., 2017; Forester and Wells, 2011; Ng et al., 2007; Presto et al., 2005; Riu-Aumatell et al., 2004). The photochemical reactions of

48 terpenes can lead to the production of tropospheric ozone, which is highly toxic to humans

(Wolkoff et al., 2000), and the formation of secondary organic aerosol with implications for
climate (Coleman et al., 2008; Lee et al., 2006; Ng et al., 2007; Vibenholt et al., 2009).

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Terpenes are also known to be emitted from building materials and household products (Allen et al., 2016), in which they are primarily used as fragrances and flavourings (Lamorena and Lee, 2008; Steinemann et al., 2011; Wang et al., 2017; Wolkoff et al., 1998), impacting indoor air quality (Nazaroff and Goldstein, 2015; Singer et al., 2006). In particular, the exposure of the public to terpenes in indoor air quality is poorly understood due to a lack of available data, despite the toxicity of their photochemical products (Jones 1999, Wolkoff and Nielsen 2001, Wang, Ang et al. 2007, Wang, Barratt et al. 2017).

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60 A variety of techniques have been used for the sampling and analysis of complex mixtures of terpenes including active and passive sorbent tube loading and desorption (Sunesson et al., 61 1999), canister sampling (Batterman et al., 1998; Pollmann et al., 2005) followed by analysis 62 using gas chromatography mass spectrometry (Birmili et al., 2003; Koch et al., 2000), proton 63 transfer reaction mass spectrometry (Holzinger et al., 2005) or other spectroscopic techniques 64 (Qiu et al., 2017). However, the accurate measurement of terpene amount fractions in indoor 65 and outdoor air is highly dependent upon the availability of appropriate SI traceable gaseous 66 PRMs (Rhoderick 2010) and analytical methods (Helmig et al., 2013). 67

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The World Meteorology Organisation (WMO) Global Atmosphere Watch (GAW) programme
is a framework to provide reliable scientific data and information on the long-term trends in
the chemical composition of the atmosphere. In WMO-GAW Report No. 171 Global Long-

- 72 Term Measurements of Volatile Organic Compounds (VOCs) new data quality objectives were
- created for priority VOC compounds including monoterpenes. These data quality objectives stipulated 20 % accuracy and 15 % precision for monoterpene measurements reported by GAW stations. Further recommendations by GAW's scientific advisory group for reactive gases have here mode to lower these data quality objectives to 5 % and renemed as uncertainty and
- been made to lower these data quality objectives to 5 % and renamed as uncertainty and repeatability (Hoerger et al., 2015). In order to meet the 5 % uncertainty target and prevent the reference material from dominating the uncertainty requires stable PRMs of monoterpenes with uncertainties of better than 1.25 % (less than a quarter of the uncertainty). There is also a requirement for performing reliable sampling or dynamic calibration methods for the in-situ calibration of instruments during field campaigns or at long-term atmospheric monitoring
- 82 stations and for independent verification of the gaseous PRMs.
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84 PRMs containing monoterpenes are challenging because monoterpenes are highly reactive compounds and can isomerise, tautomerise or react to form a wide range of other compounds 85 including other terpenes (Allahverdiev et al., 1998; Findik and Gunduz, 1997; Foletto et al., 86 87 2002). This has led to observations that the amount fraction of some monoterpenes increase overtime, including the observation of compounds that were not present when the mixture was 88 first prepared, while the amount fraction of others decline (Rhoderick and Lin, 2013). 89 Moreover, cylinder passivation (the coating applied to the internal surface of a cylinder to 90 reduce adsorptive losses) has a big impact on the stability of monoterpene gas mixtures. 91 92 Rhoderick and Lin (2013) demonstrated that specific passivation types, such as 'Experis' (Quantum) manufactured by Air Products, looked the most promising for monoterpenes. 93 94

In this paper, multicomponent monoterpene static gaseous PRMs containing α -pinene, 3carene, *R*-limonene and 1,8-cineole, as well as a mixture containing β -pinene were prepared gravimetrically at high pressure in cylinders with different internal surface passivations. The effects of adsorption to the cylinder walls and the cylinder pressure were assessed through a

99 series of decanting experiments for these different cylinder passivations. The monoterpene PRM in the most suitable cylinder passivation treatment was analysed repeatedly over a two 100 year period to assess the long-term stability building on the previous shorter-term stability 101 studies of Rhoderick et al. (Rhoderick, 2010; Rhoderick and Lin, 2013). The PRM containing 102 limonene was compared to a new dynamic system based on permeation known as Reactive Gas 103 Standard 2 (ReGaS2) developed by the Federal Institute of Metrology (METAS), (Pascale et 104 105 al., 2017), that is based on the dynamic dilution of limonene from a permeation tube to evaluate any systematic biases between the two different approaches. A portion of a monoterpene PRM 106 was decanted into a SilcoNert 2000® (Silcotek) treated sampling canisters to study the stability 107 108 and their suitability for short-term storage after field sampling.

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110 2. Experimental

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112 2.1. Gravimetric preparation of PRMs

113 PRMs containing the four monoterpenes, α -pinene (both the minus and plus optical isomers), 3-carene, *R*-limonene and 1,8-cineole, as well as one containing *n*-octane (used as an internal 114 reference standard), were prepared independently in a balance of high purity dry nitrogen 115 (BIP+, Air Products) in accordance with ISO 6142 (ISO, 2015). Each monoterpene compound 116 was prepared gravimetrically as a binary mixture (mixtures A - E) at an amount fraction of 117 nominally $5 - 10 \,\mu$ mol mol⁻¹ by liquid injection of each monoterpene, via a transfer vessel, into 118 individual 10 L evacuated cylinders (<4.0 x 10⁻⁷ mbar). A balance of high purity nitrogen 119 (BIP+, Air Products) was added by direct filling through an additional purifier (Microtorr, 120 SP600F, SAES Getters) to remove trace impurities to below < 1 nmol mol⁻¹, such as 121 hydrocarbons and water. Two β -pinene mixtures were also produced in a similar way (mixtures 122 F and G). The compound and the amount fraction of the parent PRMs were: limonene $4.968 \pm$ 123 0.044 μ mol mol⁻¹ (mixture A), \pm - α -pinene 9.942 \pm 0.029 μ mol mol⁻¹ (mixture B), 1,8-cineole 124 $5.007 \pm 0.028 \ \mu mol \ mol^{-1}$ (mixture C), 3-carene $4.954 \pm 0.036 \ \mu mol \ mol^{-1}$ (mixture D), n-125 octane 9.995 \pm 0.038 µmol mol⁻¹ (mixture E), \pm - β -pinene 9.829 \pm 0.090 µmol mol⁻¹ (mixture 126 F) and 10.492 \pm 0.175 µmol mol⁻¹ (mixture G) with all uncertainties in the gravimetric 127 preparation expanded (k = 2). 128

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All 'pure' liquid compounds were purchased from commercial suppliers (Fluka and Sigma Aldrich) and were purity analysed following the guidelines stipulated in ISO 19229:2015 by gas chromatography with a flame ionisation detector (GC-FID) prior to use. Impurities were identified and quantified by percentage area. The purity of all the monoterpenes was between 93.5 and 99.5 % (Table S1, supporting information).

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A PRM of nominally 100 nmol mol⁻¹ (mixture AA, see Table 1) containing the four 136 monoterpenes and *n*-octane was prepared by direct transfer of a portion (10 - 25 g) of each 137 gravimetrically prepared parent mixture (A - E) and topped up with a balance of filtered high 138 purity dry nitrogen (BIP+, Air Products) that was again added by direct filling through the 139 purifier. A final dilution stage was carried out to prepare a PRM at nominally 2 nmol mol⁻¹ 140 (mixture BB, Table 1). A second nominal 2 nmol mol⁻¹ mixture (mixture CC) was prepared in 141 the same way to mixture BB for the long-term stability comparison. All of the PRMs were 142 prepared in 10 litre Experis passivated cylinders from Air Products, Belgium. 143

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Table 1. Gravimetric compositions of monoterpene PRMs made by dilution of the parent
 mixtures (mixtures A-E). Amount fractions are all in nmol mol⁻¹, uncertainties in the

147 gravimetric preparation are expanded (k = 2) and do not include uncertainties arising from the

experimental validation. 148

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	Cylinder assignment					
Compound	AA	BB	CC			
limonene	93.10 ± 0.80	2.01 ± 0.02	2.04 ± 0.02			
<i>α</i> -pinene	96.10 ± 0.80	2.08 ± 0.02	2.11 ± 0.02			
1,8-cineole	94.20 ± 0.50	2.03 ± 0.01	2.07 ± 0.01			
3-carene	91.10 ± 0.70	1.97 ± 0.02	2.00 ± 0.02			
<i>n</i> -octane	89.00 ± 0.46	1.92 ± 0.01	1.95 ± 0.01			

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2.2. Analytical set-up 151

All of the measurements were performed using a GC-FID (Varian CP-3800). The system uses 152 a sample pre-concentration trap containing glass beads cooled by liquid nitrogen and held at -153 154 100 °C during sampling to collect and focus the analytes prior to injection and separation on a GC column (Varian CP-Sil 13; 75 m x 0.53 mm, phase thickness = $2.0 \,\mu$ m). All mixtures were 155 connected to the GC using SilcoNert 2000® passivated 1/16" stainless steel tubing. The lines 156 were thoroughly purged and flow rates were allowed to stabilise for at least 10 minutes before 157 commencing analysis. 158

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The PRMs were connected to the GC using a minimal dead volume connector and the flow rate 160 was set to 50 mL min⁻¹ using a custom flow restrictor. For the dynamic ReGaS2 system a flow 161 of 50 mL min⁻¹ could not be achieved. Consequently, the volume flowed across the trap was 162 recorded by a mass flow meter, calibrated with nitrogen, and subsequently corrected to match 163 the sample volume of the high pressure gas standards. Mixtures were compared by running a 164 series of up to six replicate analyses in blocks with the unknown mixture being analysed 165 between two blocks of the PRM mixture to correct for any instrumental drift during analysis. 166 The observed relative standard deviations in the peak areas of all compounds were between 0.3 167 -1.5 %. 168

2.3. Decanting experiments 169

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A schematic illustrating the decanting procedure is shown in Figure 1. The decanting 171 experiments were performed in 10 L aluminium Luxfer cylinders that had been treated with 172 different types of cylinder passivation, these included Experis, sometimes referred to as 173 Quantum (Air Products), SPECTRA-SEAL (BOC) and 'in-house' treated BOC SPECTRA-174 SEAL. It has been observed that this propriety 'in-house' passivation provides improved 175 stability for a wide range of compounds at low amount fractions. All cylinders had a 10 L 176 internal volume. Initially, a new PRM, identified as cylinder 1 in Figure 1 was prepared 177 gravimetrically (as described in Section 2.2) at an amount fraction of nominally 2 nmol mol⁻¹ 178 and a pressure of 120 bar (cylinder 1) from a dilution of a 100 nmol mol⁻¹ PRM (mixture AA). 179

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Once a new PRM (cylinder 1) had been prepared at 120 bar (day 1), the mixture was analysed 181 182 by GC-FID and compared against the reference PRM, mixture BB (day 2). The following day (day 3) approximately 50 bar of cylinder 1 was decanted by direct fill (a short well-purged 183

transfer line) to cylinder 2 leaving 70 bar in cylinder 1. Both cylinder 1 and 2 were then 184

analysed by GC-FID and compared against reference PRM, mixture BB. Finally (day 4), 185 approximately 20 bar of cylinder 2 was decanted to cylinder 3 leaving 30 bar in cylinder 2 and 186

both cylinder 2 and 3 were then analysed by GC-FID and compared against reference PRM,
mixture BB (differences in the gravimetric values between the PRM and the reference standard
were normalised). All of the cylinders were evacuated and the decant procedure was repeated
for a second time.

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All of the analyses were performed using GC-FID as described in Section 2.2. The amount 192 fraction of each compound in the decanted cylinder was determined through a comparison with 193 a nominal 2 nmol mol⁻¹ reference PRM (mixture BB). If there were no losses then the amount 194 fraction of the decanted cylinders would be the same as those of the PRM cylinder 1. Decant 195 196 losses were determined for each compound by calculating the relative difference between the amount fraction (AF_{decant}) of each compound in the decanted mixture and the expected amount 197 fraction of that compound (AF_{expected}), which was defined as its gravimetric value before any 198 199 decanting:

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201 relative difference (%) =
$$\left(\frac{AF_{decant} - AF_{expected}}{AF_{expected}}\right) \times 100$$

202

203 The amount fraction of each compound after decanting (AF_{decant}) was calculated from:

$$AF_{decant} = \frac{Area_{avgdecant}}{Area_{avgBB}} \times Grav_{BB}$$
(2)

(1)

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where, Area_{avgdecant} was the average peak area for a set of GC runs (typically five) of the decanted mixture, Area_{avgBB} was the average peak area for a set of GC runs of in-house reference PRM, mixture BB, and $Grav_{BB}$ is the gravimetrically assigned value of the compound in mixture BB.

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Figure 1: Schematic of the decanting procedure that was performed for the monoterpenes
 using 10 L Luxfer cylinders treated with different passivation types (Experis, SPECTRA-

- 216 SEAL and an in-house treated SPECTRA-SEAL).
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219 2.4. Short and long-term stability study of monoterpene PRMs

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To determine the short and long-term stability of the four component monoterpene reference 221 PRM, mixture BB was regularly analysed over a three month (75 day) period. GC peak area 222 223 responses of each terpene were ratioed to n-octane, which is known to be stable in this passivation type for more than two years (Grenfell et al., 2010) and was present in the mixtures 224 as an internal standard. The long-term stability of mixture BB (prepared on 2nd June 2015) was 225 determined by preparing a fresh nominal 2 nmol mol⁻¹ mixture (mixture CC), prepared two and 226 a half years later (904 days) on the 22nd November 2017, and comparing the peak areas and 227 their response factors. 228

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230 β -Pinene, which is known to decompose in the presence of other terpenes over time (Foletto et 231 al., 2002), was prepared at 10 µmol/mol in 2015. An independently prepared β -pinene binary 232 was prepared two and a half years later and the areas and response factors were compared to 233 determine stability.

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235 **2.5. Canister experiment**

A large number of samples are collected in the field during measurement campaigns. It is imperative that these samples can be collected and stored in a way that preserves the contents

until they are analysed. One commonly used option is the use of sampling canisters or vessels 238 that have been evacuated prior to use. It has been well documented that the use of stainless 239 steel canisters for sampling terpenes in dry or humidified air can be problematic (Batterman et 240 al., 1998; Rhoderick, 2010). Here we decant a portion of our 2 nmol mol⁻¹ in-house reference 241 PRM (mixture BB) into a SilcoNert 2000® treated 2 L sampling canister to determine their 242 suitability for short-term storage of monoterpenes. The content was analysed by GC-FID and 243 compared against the same nominal 2 nmol mol⁻¹ reference PRM (mixture BB) to determine if 244 any losses were observed over a three month period (83 days). 245

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247 2.6. ReGaS2 dynamic system

An alternative to PRM preparation in high pressure cylinders is dynamic preparation using permeation. The ReGaS2 is a mobile generator that can produce traceable reference gas mixtures of a number of species, including terpenes (Pascale et al., 2017).

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The method is based on permeation and subsequent dynamic dilution: a permeation tube containing the pure terpene is stored in an oven used as permeation chamber. The pure substance permeates at a constant rate into the matrix gas and can be diluted to give the desired amount fraction. The mass loss over time of the permeation tube is precisely calibrated using a traceable magnetic suspension balance. All parts in contact with the reference gas are coated with SilcoNert2000[®].

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The ReGaS2 mobile gas generator was fitted with a limonene permeation tube and set to dynamically generate an output of nominally 4 nmol mol⁻¹. The amount fraction of the limonene produced by the dynamic system was measured using the same analytical set-up as described in Section 2.2 and compared to our nominal 2 nmol mol⁻¹ reference PRM (mixture BB).

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266 **2.7. Uncertainty calculations**

The evaluation of measurement uncertainty was in accordance to the 'Guide to the expression of uncertainty in measurement' (Joint Committee for Guides in Metrology, 2008).

In the supplementary section there is a description of an uncertainty evaluation when
comparing the response of an unknown mixture against a validated calibration standard e.g. a
PRM (Eq. S1 – S4).

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274 **3. Results and discussion**

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277 3.1. Decanting experiments and selection of passivation treatment for long-term stability 278 measurements

The adsorption of the monoterpenes to the internal surfaces of the cylinder and valve were investigated through a series of decanting experiments as detailed in Section 2.3. The results for the different passivation types at 120 bar are shown in Figure 2. There is a tabulated summary of the results of the decanting experiments in Tables S2 - S7.

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Figure 2: The relative difference between the amount fraction of the decanted mixtures and
the expected amount fraction based on gravimetric value of the mixture before any decanting.
Each decant was performed twice for each passivation type.

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Decant losses of monoterpenes in the 10 L cylinders internally passivated with Air Products 290 Experis treatment were minimal (Tables S2 and S3). No statistically significant differences 291 were observed, therefore it can be confirmed, in agreement with Rhoderick et al. (Rhoderick 292 and Lin, 2013) that Experis cylinders are the most suitable for containing monoterpene PRMs. 293 Figure 3 shows that the amount fraction does not appear to be influenced by the pressure within 294 the cylinder, down to low pressure at 30 bar, as all agree within the measurement uncertainty 295 and there is no overall directional trend. Below 30 bar we observe that the ratio is less than 1 296 for all components. While the results are within the measurement uncertainty, wall factors 297 could have an influence on composition at low pressures (< 30 bar) (Brewer et al., 2018). As 298 reported in Brewer et al. (2018) compounds adsorbed to the walls at high pressure were 299 observed to desorb back into the gas phase at lower pressures. 300

302 Figure 2 and Tables S3 and S4, show the initial decant, and repeat decant at 120 bar, in 10 L cylinders passivated internally with BOC SPECTRA-SEAL treatment. Aside from the *n*-octane 303 a significant decrease in the amount fraction of all monoterpenes was observed (except for 304 limonene in the first decant) relative to the reference PRM (BB). No further decants were 305 performed for this cylinder type as the passivation was shown to be unsuitable for 306 307 monoterpenes, with strong degradation observed by GC (Figure 4) within less than 24 hours after making the initial PRM. In an attempt to improve the stability of trace monoterpenes in 308 SPECTRA-SEAL passivated cylinders, further in-house treatment was applied to a new set of 309 310 cylinders. The results of this are shown in Figure 2 and Tables S5 and S6, however no improvement was observed and all of the monoterpenes showed significant losses when the 311 PRM was analysed by GC, less than 24 hours after preparation. 312

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Figure 3: The relationship between cylinder pressure and monoterpene amount fraction after normalisation to *n*-octane.

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To investigate potential degradation components, a sample of a monoterpene mixture in an internally treated SPECTRA-SEAL cylinder was loaded onto a set of Chromasorb-106 and

321 Tenax sorbent tubes (both packed in-house) and analysed on a Thermal-Desorption Gas Chromatograph Mass Spectrometer (TD-GC-MS). Similarly, a portion of the reference PRM 322 (mixture BB) was also loaded onto Chromasorb-106 and Tenax sorbent tubes and analysed by 323 TD-GC-MS. Five major peaks were consistently observed in the chromatograms of the 324 desorbed tubes (Figure 4). The additional peaks observed in the sample from the SPECTRA-325 SEAL cylinder were identified as the following monoterpenes: (a) α -terpinene, (b) τ -terpinene, 326 (c) terpinolene, (d) cymene and (e) camphene based on retention time and MS library matching 327 to the NIST database. Mass spectrometry was used for compound identification and good 328 329 forward match (FM) and reverse match (RM) values, predominantly >900 and all above 860 were obtained (see Tables S8 and S9 for details of the elution times, FM and RM values and 330 331 Figure S1 for mass spectra).

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Interestingly, α -terpinene is produced industrially by acid-catalysed rearrangement of α -pinene and camphene by oxidation of α -pinene (Findik and Gunduz, 1997), which had disappeared from the SPECTRA-SEAL passivated cylinders after 24 hours (Figure 4). No other terpenes or peaks were observed in the sample of the reference PRM (mixture BB) except for the expected α -pinene, 3-carene, *R*-limonene and 1,8-cineole and *n*-octane. Kovats' Retention Indices were used to confirm the assignment of terpene compounds (Table S10 and Figure S2).



Figure 4: Typical chromatograms for a stable (pink) and an unstable (grey) terpene mixture.
The nominally 2 nmol mol⁻¹ reference PRM, mixture BB (shown in pink) in an Air Products
Experis cylinder was made from the same parent PRM as the PRM made in the internally

passivated BOC SPECTRA-SEAL cylinder (shown in grey). The SPECTRA-SEAL cylinder was analysed less than 24 hours after preparation and shows significant degradation of the terpene compounds. The zoomed in portion of the chromatogram focuses on the α -pinene peak (inset), showing that all of this compound has been lost. The additional peaks observed in the analysis of the SPECTRA-SEAL passivated cylinder, labelled as a – e, correspond to those named in the main text and to the observed MS shown in Figure S1.

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352 **3.2. Short- and long-term stability study of monoterpene PRM**

The short-term and long-term stability of mixture BB was determined through a series of experiments as detailed in Section 2.4. Over the first three month period that mixture BB was analysed the ratio of the monoterpene to *n*-octane remains constant within the measurement uncertainty. Regression analysis using a least squares fit shows that the gradients for all four monoterpenes are within the measurement uncertainty of zero showing no statistically significant change in amount fraction over the 75 day timeframe.



Figure 5: The short-term stability of reference PRM (mixture BB) at nominally 2 nmol mol⁻¹ compared as a ratio of the area of each monoterpene normalised relative to the *n*-octane internal standard. Error bars are included to account for the relative standard deviation of the mean (k= 2). The solid lines show the results of a linear least squares fitting routine with the shaded area showing the confidence interval (95 %) of the fit.

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Mixture BB was prepared on 2nd June 2015 and mixture CC was more than two years later (904 367 days) on the 22nd November 2017. A set of measurements were run to compare mixture BB 368 and CC. This was repeated twice in the space of two days. Gravimetric values were normalised 369 and the peak areas of the monoterpenes were then compared and the differences recorded 370 (Table 2). It was found that, unsurprisingly, n-octane shows the best agreement and smallest 371 372 difference, however all the monoterpenes agreed well and differences were no greater than 2.5 % between mixtures BB and CC. The relative standard deviations of the peak areas was 373 between 0.1 - 1.5 % with the larger relative standard deviations correlating to the highest 374 differences between the gas mixtures suggesting that the measurement is one of the largest 375 sources of uncertainty in the experimental differences. The comparison infers that the 376 monoterpene mixtures in Experis treated cylinders are stable for over two and a half years. 377

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379 Mixture F and G containing β -pinene were prepared 976 days apart (approximately 2 years and 380 8 months difference), and were compared. Agreement for β -pinene, once normalised to take into account gravimetric differences, was better than 0.5 % and the relative standard deviation 381 382 in the peak areas were 0.7 - 1.1 %. No systematic bias was observed. This suggests that in Experis treated cylinders there is little or no decay of β -pinene at the μ mol/mol level when 383 prepared as a binary mixture. Stability has been demonstrated for greater than two and a half 384 385 years suggesting that it is the interaction of β -pinene with other monoterpenes in multicomponent gas standards that is the likely cause of their degradation. 386

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Table 2: Comparison showing the percentage difference between PRM mixtures prepared more than two years apart to assess the long-term stability of mixture BB and mixture F. Gravimetric values were normalised and the peak areas compared. There are two columns for the comparison of mixture BB and CC as the comparison was repeated on two consecutive days.

	The difference when comparing PRMs					
Compound	Mixture	BB v CC	Mixture F v G			
limonene	0.24 %	0.94 %				
<i>α</i> -pinene	0.06 %	1.61 %				
1,8-cineole	1.96 %	-0.22 %				
3-carene	-0.75 %	1.35 %				
β -pinene			0.45 %			
<i>n</i> -octane	-0.75 %	0.24 %				

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395 3.3. Short-term stability of monoterpenes in treated sampling canisters

Field campaign measurements require the short-term storage of VOC samples. Sampling canisters made from electropolished steel are frequently used despite losses being observed (Batterman et al., 1998). Another solution is to use SilcoNert 2000® treated canisters (silanisation treatment, Silcotek). However, the SPECTRA-SEAL cylinders that performed poorly in the decant experiments, also use a silanisation surface treatment, therefore it was
important to determine the suitability of SilcoNert 2000® treated canisters for short-term
storage of monoterpenes. Following decant of mixture BB into the SilcoNert 2000® treated
canister the contents were compared against mixture BB after 1, 8 and 83 days. The results of
this are shown in Figure 6.

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409 **Figure 6:** The short-term stability of mixture BB decanted into a SilcoNert 2000® treated 410 canister compared as a ratio of the area of each monoterpene normalised relative to the *n*-octane 411 internal standard. Error bars are included to account for the relative standard deviation of the 412 mean (k = 2).

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No statistically significantly trends were observed for the stability although higher than normal relative standard deviations in the GC peak areas were observed (≤ 4 % for all components except 1,8-cineole which was ≤ 8 %). This can be attributed to changes in the flow of gas from the canister samples during measurement due to the small volume and thus the decreasing pressure of the gas contained.

It appears that unlike the SPECTRA-SEAL passivated cylinders, the SilcoNert 2000® treated 420 canisters would allow the storage of multi-component monoterpene standards for up to three 421 422 months and still meet the data quality objective criteria recommended by GAW and its scientific advisory group (Hoerger, Claude et al. 2015). Nevertheless, this does not mean that 423 a whole air sample containing terpenes or a broad array of terpenes together would behave in 424 425 the same way due to the impact of humidity, therefore more work is required to determine this. However, it would suggest that decanting of PRMs for transport into the field in small 426 SilcoNert 2000® treated canister should be possible. 427

428 3.4. Comparison of dynamic and static PRM

429 Two SI traceable preparation techniques for producing reference gas mixtures were compared. 430 One was the preparation of static gravimetric PRMs, the other the generation of a dynamic reference standard from ReGaS2 using a permeation tube. From the weighing of the limonene 431 permeation tube and from the data that was logged for the nitrogen flow and subsequent 432 433 dilution it was calculated that the ReGaS2 mobile gas generator was outputting 4.41 ± 0.32 nmol mol⁻¹ of limonene with an expanded uncertainty of 7.3 % (k = 2). Using the PRM static 434 standards gravimetrically produced the output of the ReGaS2 dynamic system was estimated 435 to be 3.57 ± 0.11 nmol mol⁻¹ of limonene with an expanded uncertainty of 2.9 % (k = 2). 436

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The static PRM that was used in this comparison (mixture BB) was also one of the mixtures used as part of the CCQM-K121 monoterpene key comparison at nominally 2.5 nmol mol⁻¹ Results from CCQM-K121 demonstrated that all of the participants (Korea Research Institute of Standards and Science, KRISS; National Institute of Standards and Technology, NIST; and NPL) agree within the k = 2 expanded uncertainties for all of the monoterpenes evaluated, including limonene.

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One of the reasons for the systematic bias between the two approaches can be attributed to the 445 temperature at which the permeator was operated, as the temperature was observed to have a 446 strong influence on the reproducibility of the permeation rate. At lower temperatures, such as 447 30°C (which was the temperature used for the comparison), the permeator does not reach a true 448 steady state and it was observed that the variability on the permeation rate for the same 449 temperature between two measurements was between 8 and 10 %. A shift in the permeation 450 rate of this magnitude coupled to uncertainties in temperature would be enough to compensate 451 452 for the systematic bias observed between the two approaches.

453

454 The second reason is the 15-20 % decrease in the permeation rate. To investigate this further 455 the permeation rate of limonene from the ReGaS2 dynamic system was measured over an 11 month period between March 2017 and February 2018. The decrease in the permeation rate 456 was determined to be 35 % over this temporal period (Figure S3) for the same temperature. 457 The measurement of the permeation rate in the magnetic suspension balance lasted between 458 two and seven days with an associated uncertainty between 0.5 and 1.5 % for one measurement 459 at one temperature thus suggesting that the uncertainty assigned to ReGaS2 during the 460 comparison was too low. 461

462

A decrease in the permeation rate of this magnitude coupled to the high uncertainties at such low temperatures would be enough to compensate for the systematic bias observed between the two approaches. Despite the systematic bias observed between the two methods at this trace level, the results of this first comparison are encouraging and show that state-of-the-art 467 developments are being made with dynamic systems capable of delivering reliable outputs468 suitable for calibrating systems in the field.

469 470

471 **4.** Conclusions

In this paper we have investigated the short-term and long-term stability of monoterpenes in differently internally passivated cylinders. The choice of cylinder passivation is critically important in the preparation of monoterpene gas mixtures. We have demonstrated that Experis treated cylinders are the most appropriate for containing low amount fraction monoterpene PRMs and that the amount fraction is not influenced by pressure between 30 and 120 bar.

477

The need for suitable storage and transport of PRMs into the field has driven us to investigate the suitability of using SilcoNert 2000® treated canisters for monoterpenes. It was discovered that SilcoNert 2000® treated canisters could hold monoterpenes for up to three months with an uncertainty of 10 %, in line with GAW data quality objectives.

482

483 We compared the ReGaS2 dynamic mobile generator against high pressure static PRMs gravimetrically prepared at NPL. It was found that the output of limonene from dynamic 484 ReGaS2 was 15 - 20 % lower than calculated. These differences correspond to less than 0.5 485 nmol mol⁻¹ and it has been suggested that the bias may be attributed to the reproducibility of 486 the limonene permeator at low temperature due to the permeation rate not reaching equilibrium. 487 This first comparison of a dynamic terpene standard against a traditional static standard is the 488 first step in providing the community with traceable reference materials suitable for in the field 489 measurements to meet GAW data quality objectives. 490

491

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- 497
- 498

499 **5. References**

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647 648	Supplement of "The importance of cylinder passivation for preparation and long-term stability of multicomponent monoterpene primary reference materials"
649	
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669 **Description of uncertainty analysis procedure**

Below is the uncertainty evaluation adopted when comparing the response of an unknownmixture against a validated calibration standard e.g. a PRM:

$$\bar{\mathbf{r}} = \frac{2A_{u,avg}}{(A_{s,avg1} + A_{s,avg2})} \tag{S1}$$

674

Where \bar{r} is the average ratio, $A_{u,avg}$ is the average peak area from n repeated measurements of the comparison mixture, $A_{s,avg1}$ is the average peak area from n repeated measurements of the calibration standard before running the comparison mixture and $A_{s,avg2}$ is the average peak area from n repeated measurements of the calibration standard after running the comparison mixture.

680

681 The amount fraction of the target component in the comparison mixture, x_u , is then calculated 682 by:

$$x_u = x_s \bar{r} \tag{S2}$$

684

685 Where x_s is the amount fraction of the target component in the standard. The standard 686 uncertainty of the measurand, $u(x_u)$, is calculated by:

687

688
$$\frac{u(x_u)}{x_u} = \sqrt{\frac{u(x_s)^2}{x_s^2} + \frac{u(\bar{r})^2}{\bar{r}^2}}$$
(S3)

689

690 $u(x_s)$ is the uncertainty of the reference standard $u(\bar{r})$ is the uncertainty of the ratio, it includes 691 e.g. repeatability, internal blanks, peak shape (error of integration), error in the sample 692 volume. The uncertainty in \bar{r} is calculated by:

694

693
$$\frac{u(\bar{r})^{2}}{\bar{r}^{2}} = \frac{u(A_{u,avg})^{2}}{A_{u,avg}^{2}} + \frac{u(A_{s,avg1})^{2}}{(A_{s,avg1} + A_{s,avg2})^{2}} + \frac{u(A_{s,avg1})^{2}}{(A_{s,avg1} + A_{s,avg2})^{2}}$$
(S4)

695

698	
699	

	Chemical purity analysed							
Compounds	+-α-	α-	limone	3-	1,8-	<i>n</i> -	+-β-	β-
found	pinene	pinene	ne	carene	cineole	octane	pinene	pinene
±α-pinene	97.95%	98.80%	<0.01%	0.02%	0.03%	<0.01%	1.61%	1.08%
±β-pinene	0.06%	0.11%	<0.01%	0.02%	0.03%	<0.01%	93.82%	95.33%
limonene	0.17%	0.24%	99.04%	0.24%	0.34%	<0.01%	1.48%	0.87%
3-carene	<0.01%	<0.01%	<0.01%	98.23%	<0.01%	<0.01%	<0.01%	<0.01%
1,8-cineole	<0.01%	<0.01%	<0.01%	<0.01%	99.49%	<0.01%	<0.01%	<0.01%
3-carene	<0.01%	<0.01%	<0.01%	<0.01%	0.01%	<0.01%	<0.01%	<0.01%
cis-ocimene	0.01%	0.03%	0.02%	<0.01%	<0.01%	<0.01%	<0.01%	<0.01%
myrcene	<0.01%	<0.01%	0.01%	<0.01%	<0.01%	<0.01%	<0.01%	<0.01%
<i>n</i> -octane	<0.01%	<0.01%	<0.01%	<0.01%	<0.01%	99.90%	<0.01%	<0.01%
unknown	0.60%	0.42%	0.30%	0.96%	0.04%	<0.01%	3.07%	2.71%
terpene								
other	1.21%	0.27%	0.63%	0.53%	0.06%	0.10%	0.02%	0.03%
hydrocarbons								

701

Table S2: The percentage difference between the reference standard mixture BB and

Table S1: Overview of purity analysis of chemicals purchased.

the decanted monoterpene mixture in a 10 L internally passivated Experis cylinder

704 (normalised for gravimetric differences).

Experis		Difference with respect to the reference standard mixture BB					
			+/- α-			1,8-	
Decant	Pressure	<i>n</i> -octane	pinene	3-carene	R-limonene	cineole	
cylinder 1	120 bar	0.0%	0.0%	0.6%	0.7%	0.5%	
cylinder 1	70 bar	0.7%	0.4%	0.3%	0.9%	0.9%	
cylinder 2	50 bar	0.7%	0.3%	0.2%	0.9%	0.8%	
cylinder 2	30 bar	0.6%	0.0%	0.3%	0.9%	1.7%	
cylinder 3	20 bar	0.3%	-0.8%	-0.6%	-0.4%	-1.1%	

705 706

Table S3: The percentage difference between the reference standard mixture BB and

the decanted monoterpene mixture in a 10 L internally passivated Experis cylinder

repeated (normalised for gravimetric differences).

Experis repeat		Differenc	Difference with respect to the reference standard mixture BB					
			+/- α-			1,8-		
Decant	Pressure	<i>n</i> -octane	pinene	3-carene	R-limonene	cineole		
cylinder 1	120 bar	0.5%	0.7%	0.9%	1.4%	1.5%		
cylinder 1	70 bar	0.5%	0.8%	0.8%	0.6%	0.8%		
cylinder 2	50 bar	0.3%	0.6%	0.5%	0.9%	1.0%		
cylinder 2	30 bar	0.1%	-0.1%	0.0%	-0.2%	-0.1%		
cylinder 3	20 bar	0.6%	0.4%	0.3%	0.5%	-0.2%		

- 711 **Table S4:** The percentage difference between the reference standard mixture BB and
- the decanted monoterpene mixture in a 10 L internally passivated BOC SPECTRA-
- 713 SEAL cylinder (normalised for gravimetric differences).
- 714

BOC SPECT	RA-SEAL	Difference	e with respect to the reference standard mixture BB				
			+/- α-			1,8-	
Decant	Pressure	<i>n</i> -octane	pinene	+3-carene	R-limonene	cineole	
cylinder 1	120 bar	0.3%	-61.8%	-2.0%	8.5%	-20.4%	
cylinder 1	70 bar						
cylinder 2	50 bar	No furthe	r decants were	performed fo	r this cylinder	type as the	
cylinder 2	30 bar	passivation was shown to be unsuitable for monoterpenes.					
cylinder 3	20 bar	-				-	

- **Table S5:** The percentage difference between the reference standard mixture BB and
- the decanted monoterpene mixture in a 10 L internally passivated BOC SPECTRA-
- 719 SEAL cylinder (normalised for gravimetric differences) repeated.
- 720

BOC SPECTRA-SEAL repeat		Difference with respect to the reference standard mixture BB					
Decant	Pressure	<i>n</i> -octane	+/- α- pinene	+3-carene	R-limonene	1,8- cineole	
cylinder 1	120 bar	0.4%	-100.0%	-26.5%	-53.5%	-52.0%	
cylinder 1	70 bar						
cylinder 2	50 bar	No furthe	r decants were	performed fo	r this cylinder	type as the	
cylinder 2	30 bar	passivation was shown to be unsuitable for monoterpenes.					
cylinder 3	20 bar	-				-	

721

722

723 **Table S6:** The percentage difference between the reference standard mixture BB and

the decanted monoterpene mixture in a 10 L internally passivated treated BOC

725 SPECTRA-SEAL cylinder with further proprietary in-house treatment (normalised

726 for gravimetric differences).

In-house treated BOC SPECTRA-SEAL		Difference with respect to the reference standard mixture BB					
			+/- α-			1,8-	
Decant	Pressure	<i>n</i> -octane	pinene	+3-carene	R-limonene	cineole	
cylinder 1	120 bar	0.7%	-100.0%	-27.8%	-48.8%	-54.9%	
cylinder 1	70 bar						
cylinder 2	50 bar	No furthe	r decants were	performed fo	r this cylinder	type as the	
cylinder 2	30 bar	passivation was shown to be unsuitable for monoterpenes.					
cylinder 3	20 bar	1				1	

730 **Table S7:** The percentage difference between the reference standard mixture BB and

the decanted monoterpene mixture in a 10 L internally passivated treated BOC

732 SPECTRA-SEAL cylinder with further proprietary in-house treatment (normalised

733 for gravimetric differences) repeated.

734

In-house treated BOC SPECTRA-SEAL repeat		Difference with respect to the reference standard mixture BB					
D	D		+/- α-	. 2	DĽ	1,8-	
Decant	Pressure	<i>n</i> -octane	pinene	+3-carene	K-IImonene	cineole	
cylinder 1	120 bar	0.1%	-100.0%	-94.9%	-94.5%	-97.4%	
cylinder 1	70 bar						
cylinder 2	50 bar	No furthe	r decants were	performed fo	r this cylinder	type as the	
cylinder 2	30 bar	passivation was shown to be unsuitable for monoterpenes.					
cylinder 3	20 bar	-				-	

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- 737 Table S8: Elution times, forward match (FM) and reverse match (RM) values obtained by
- mass spectrometry for Mixture BB.

1 7								
Mixture BB								
Compound	Elution time	Forward match	Reverse match					
α-pinene	39.25	904	907					
3-carene	41.25	909	952					
limonene	41.65	894	896					
1,8-cineole	41.80	864	900					

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Table S9: Elution times, forward match (FM) and reverse match (RM) values obtained by
 mass spectrometry for a terpene mixture in a BOC SPECTRA-SEAL passivated cylinder.

Mixture in BOC SPECTRA-SEAL passivated cylinder										
Compound	Elution time	Forward match	Reverse match							
camphene	39.80	946	962							
a-terpinene	41.40	921	930							
cymene	41.65	937	949							
τ-terpinene	42.25	911	931							
terpinolene	43.05	938	945							

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746 **Table S10:** The Kovats' Retention Indices on a non-polar column, using a custom temperature

program for reference publications 1-8 (Adams, 1998; Araujo et al., 2003; de Marchese et al.,

2007; Dwivedi et al., 2004; Frizzo et al., 2001; Novak et al., 2001; Riu-Aumatell et al., 2004;
Tuberoso et al., 2005).

		Kovats' Retention Indicies value											
Elution time	Compound	1	2	3	4	5	6	7	8	Average	Max value	Min value	
39.25	α-pinene	938	937	933		928	934	938	939	935	939	928	
39.80	camphene	954		946		955		954	953	952	955	946	
41.25	3-carene			1011			1011	1013	1011	1012	1013	1011	
41.40	α -terpinene		1017			1024		1020	1018	1020	1024	1017	
41.65	p-cymene	1025	1026			1015	1023		1023	1022	1026	1015	
41.66	limonene	1029	1029	1020	1017	1028	1029	1034	1031	1027	1034	1017	
41.80	1,8-cineole		1033	1020			1036	1031		1030	1036	1020	
42.25	γ-terpinene		1058	1051	1057	1058	1059	1063	1062	1058	1063	1051	
43.05	terpinolene		1084	1097	1074	1086	1088	1092	1088	1087	1097	1074	



752 753 **Figure S1:** Mass spectrometry ion fragmentation spectra for (a) camphene (b) α -terpinene (c) 754 cymene (d) *τ*-terpinene (e) terpinolene peaks identified and observed in a BOC SPECTRA-755 SEAL passivated cylinder.



Figure S2: The average Kovats' Retention Indices on a non-polar column, using a custom temperature program for reference publications 1-8 (Adams, 1998; Araujo et al., 2003; de
Marchese et al., 2007; Dwivedi et al., 2004; Frizzo et al., 2001; Novak et al., 2001; Riu-Aumatell et al., 2004; Tuberoso et al., 2005). Error bars cover the range from minimum to maximum for the Kovats' Retention Indice values.



Figure S3: The permeation rate of limonene measured in the magnetic suspension balance over
 an 11 month period at 30°C with a nitrogen flow of 0.17 l/min.